Benzofuran-2-one

The invention relates to novel benzofuran-2-ones, to processes for preparing them and to their use as colorants for organic materials, especially organic materials of high or low molecular weight.

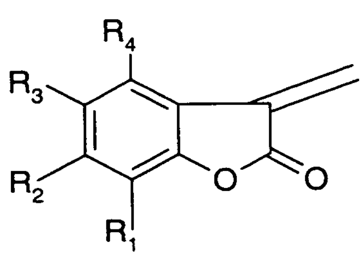
Benzofuran-2-ones as stabilizers for polymers are known, for example, from WO 80/01566. EP-A-921 435 discloses benzofuran-2-ones. EP-A-632 102 discloses that benzofuran-2-ones can be used for the mass colouring of plastics. These products, however, go only part-way towards meeting the present-day requirements in terms of application properties.

The object of the present invention was therefore to provide benzofuran-2-ones which in particular possess good solubilities in addition to giving good performance properties such as heat and light fastness and strong, transparent and bright colorations. The object was further to provide an economic process for preparing the novel benzofuran-2-ones, in accordance with the present-day requirements of an environmental process.

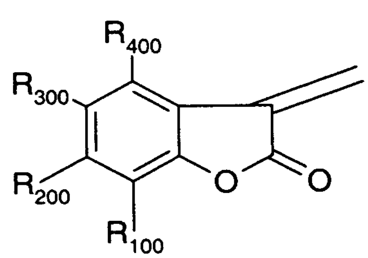
The present invention accordingly provides compounds of the formulae (Ia), (Ib) or (Ic)

$$Q_1{=}X_1 \quad (Ia) \qquad Q_1{=}X_2{=}Q_1 \quad (Ib) \qquad Q_1{=}X_2{=}Q_2 \quad (Ic)$$

in which
Q_1 is a benzofuran-2-one of the formula (IIa), and
Q_2 is a benzofuran-2-one of the formula (IIb)



(IIa)



(IIb)

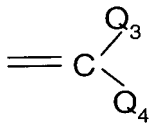
in which

R_1, R_2, R_3, R_4, R_{100}, R_{200}, R_{300} or R_{400} independently of one another are hydrogen, halogen,

hydroxyl, cyano, ether, nitro, an amine, amide, imine, urethane, sulfonamide, ester, carboxylic acid or sulfonic acid radical or carboxylic salt, sulfonic salt or substituted or unsubstituted C_1-C_{24}alkyl, C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, C_6-C_{24}aryloxy, C_6-C_{24}arylthio, A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy or A_5-A_{18}heteroarylthio, or

R_1 and R_2, R_2 and R_3, R_3 and R_4 or R_{100} and R_{200}, or R_{200} and R_{300}, R_{300} and R_{400}, independently of one another in each case together are divalent, substituted or unsubstituted radicals, such as polycyclic radicals or 1,3-butadien-1,4-ylene or -CH=CH-NH-, the two last radicals forming an additional fused-on 5- or 6-membered ring, and

X_1 is a hydrazone or imine radical, with the proviso that, if R_1, R_2, R_3 and R_4 are hydrogen, or one R_1, R_2, R_3 or R_4 is methyl, the hydrazone radical is excluded, or, if R_1, R_2, R_3 or R_4 is hydrogen, X_1 is not phenylimine- or 4-dimethylamine-phenylimine,
or X_1 is a methylene radical,

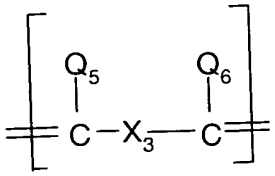


in which
Q_3 and Q_4 independently of one another are hydrogen or substituted or unsubstituted C_1-C_{24}alkyl, -CO-(C_1-C_{24}alkyl), -CO-O-(C_1-C_{24}alkyl), C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24} alkenyl, C_6-C_{24}aryl, -CO-O-(C_6-C_{24}aryl), -CO-(C_6-C_{24}aryl), C_6-C_{24}aryloxy, a primary or secondary amine radical, C_6-C_{12}arylthio, C_7-C_{25}aralkyl, A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy or A_5-A_{18}heteroarylthio, or
Q_3 and Q_4 together are a lactam, quinomethylene, hydantoin, acenaphthenequinone, azlactone, pyrazolonyl, barbituric acid, isoindolinone or isoindoline radical, with the proviso that Q_3 and Q_4 are not phenyl or
Q_3 is not hydrogen and Q_4 is not methyl, 4-aminophenyl, 4-dimethylaminophenyl or -OCO-4-(1-chlorophenylene) if R_1, R_2, R_3 and R_4 are hydrogen, or Q3 is not hydrogen and Q_4 is not 4-aminophenyl if R_1 and R_3 are tert-C_5H_{11}alkyl, or Q_3 is not hydrogen and Q_4 is not 2-hydroxyphenyl if R_1 and R_3 are tert-butyl, or
Q_3 is not hydrogen and Q_4 is not a primary or secondary amine radical if R_3 is hydrogen, methoxy or hydroxyl and R_1, R_2 and R_4 are hydrogen,
or Q_3 is not hydrogen and Q_4 is not a secondary amine radical if R_1, R_2, R_3 and R_4 are

hydrogen,

and

X_2 is a tetravalent 5- or 6-membered heterocyclic ring,

or is 

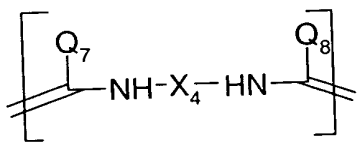
in which

X_3 is a single bond, unsubstituted or substituted C_6-C_{24}arylene, A_5-A_{18}heteroarylene, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene or naphthylene, or a tetravalent polyether, polyimine, polyamine radical, or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, $-CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, $-NR_{42}CO$-, $-CONR_{42}$-, -O-, -S-, -SO-, $-SO_2$- or $-NR_{42}$-, in which

R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24} alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl or A_5-A_{18}heteroaryl, and

Q_5 and Q_6 independently of one another are hydrogen, C_6-C_{24}aryl, C_6-C_{24}aryloxy, C_1-C_{24}alkyl, C_1-C_{24} alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_6-C_{24}aryloxy, C_6-C_{24}arylthio or A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy, A_5-A_{18}heteroarylthio,

or

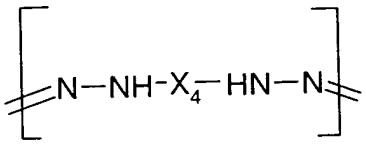
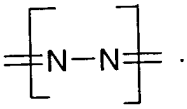
X_2 is 

in which

Q_7 and Q_8 independently of one another are Q_5 or Q_6, and

X_4 is C_6-C_{24}arylene, A_5-A_{18}heteroarylene,a polymethylidene or divalent polyether, polyimine, polyamine radical, or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -$NR_{42}CO$-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-,

or

X_2 is  or  .

The invention also embraces tautomeric and polymorphic structures of the compounds of the formula (Ia), (Ib) or (Ic).

In one preferred embodiment of the invention, R_1, R_2, R_3, R_4, R_{100}, R_{200}, R_{300} or R_{400} independently of one another are hydrogen, halogen, hydroxyl, cyano, NO_2, NR_5R_6, NR_7COR_5, NR_7COOR_5, $N=CR_5R_6$, $CONR_7R_8$, OR_5, $COOR_5$, (C_1-C_{12}alkyl)-$COOR_5$, COO^-X^+, SR_5, SOR_5, SO_2R_5, $SO_2NR_7R_8$, SO_3R_5 or $SO_3^-X^+$, or are unsubstituted or mono- or poly-halogen-, -hydroxyl-, -$COOR_6$-, or -COO^-X^+ -substituted C_1-C_{18}alkyl, C_5-C_{16}cycloalkyl, which can be uninterrupted or interrupted one or more times by O or NR_6 or are A_5-A_{12}heteroaryl, C_7-C_{18}aralkyl, C_6-C_{10}aryl or C_1-C_6alkyl unsubstituted or substituted one or more times by halogen, nitro, OR_6, SR_6, NR_7R_8, $CONR_7R_8$, $COOR_6$, COO^-X^+, $SO_2NR_7R_8$, $SO_3^-X^+$ or NR_7COR_6, or

R_1 and R_2, R_2 and R_3, R_3 and R_4, or R_{100} and R_{200}, or R_{200} and R_{300}, R_{300} and R_{400}, are, for example, divalent substituted or unsubstituted radicals, such as 1,3-butadien-1,4-ylene, or -CH=CH-NH- which form an additional fused-on 5- or 6-membered ring,

R_5 is unsubstituted or mono- or poly-halogen-, -hydroxyl-, -oxo-, -cyano-, -$COOR_6$- or -COO^-X^+-substituted C_1-C_{25}alkyl, C_5-C_{12}cycloalkyl or C_2-C_{24}alkenyl which can be uninterrupted or interrupted one or more times by O, S or NR_6, or is A_5-A_{18}heteroaryl, C_7-C_{18}aralkyl or C_6-C_{18}aryl unsubstituted or substituted one or more times by halogen, nitro, cyano, OR_6, SR_6, NR_7R_8, $CONR_7R_8$, $COOR_6$, COO^-X^+, SO_2R_6, $SO_2NR_7R_8$, SO_3R_6, $SO_3^-X^+$, NR_7COR_6 or NR_7COOR_6,

R_6 is hydrogen, unsubstituted or mono- or poly-halogen-, -hydroxyl-, -oxo- or -cyano-substituted C_1-C_{25}alkyl or C_2-C_{24}alkenyl which can be uninterrupted or interrupted one or more times by O, S or NR_7, or is A_5-A_{18}heteroaryl, C_7-C_{18}aralkyl or C_6-C_{18}aryl unsubstituted or substituted one or more times by halogen, nitro, cyano, hydroxyl, OR_7, SR_7, NR_7R_8, $CONR_7R_8$, $COOR_7$, COOH or $COO^- X^+$,

R_7 and R_8 independently of one another are hydrogen, C_6-C_{18}aryl, C_7-C_{18}aralkyl, unsubstituted or mono- or poly-halogen-, -hydroxyl- or -C_1-C_{18}alkyl-, or C_1-C_{12}alkoxy-substituted C_1-C_{24}alkyl, C_6-C_{14}aryl, C_7-C_{16}aralkyl or C_2-C_{24}alkenyl, or

R_7 and R_8 together with the nitrogen are unsubstituted or mono- to tetra-C_1-C_4alkyl-substituted pyrrolidine, piperidine, piperazine or morpholine, or are carbazole, phenoxazine or phenothiazine,

X^+ is an alkali metal cation such as Li^+, Na^+, K^+ or an alkaline earth metal cation such as $Mg^{++}{}_{1/2}$, $Ca^{++}{}_{1/2}$, $Sr^{++}{}_{1/2}$, $Ba^{++}{}_{1/2}$ or cations from Group 11 of the IUPAC form of the Periodic Table such as Cu^+, $Cu^{++}{}_{1/2}$ or from Group 12 of the IUPAC form of the Periodic Table such as $Zn^{++}{}_{1/2}$ or from Group 13 of the IUPAC form of the Periodic Table such as $Al^{+++}{}_{1/3}$, or an ammonium radical $[NR_7R_8R_{10}R_{11}]^+$, and

R_{10} and R_{11} independently of one another are hydrogen, C_1-C_{24}alkyl, C_5-C_{24}aryl or C_7-C_{25}aralkyl.

Preferably, at least one R_1, R_2, R_3, R_4, R_{100}, R_{200}, R_{300} or R_{400} independently of one another are C_3-C_{25}alkyl, which can be branched or unbranched, and also are hydroxyl, or R_1 and R_2, R_2 and R_3, R_3 and R_4 or R_{100} and R_{200}, or R_{200} and R_{300}, R_{300} and R_{400}, independently of one another in each case together are divalent radicals, such as polycyclic radicals or 1,3-butadiene, 1,4-ylene or -CH=CH–NH-, the latter resulting in an additional fused-on 5- or 6-membered ring, and in a further preferred embodiment of the invention are substituted by hydroxyl.

A further preferred embodiment of the present invention comprises the compounds of the formula (Ia) in which at least two of the substituents R_1, R_2, R_3 or R_4 are not hydrogen, preferably R_1 and R_3 are not hydrogen and, with particular preference, R_1 and R_3 independently of one another are COOH or COO(C_1-C_{12}alkyl)-substituted or unsubstituted C_1-C_8alkyl or C_1-C_8alkoxy, and, with very particular preference, R_1 and R_3 independently of one another are C_1-C_4alkyl which is unsubstituted or substituted by COOH or

COO(C_1-C_4alkyl), in particular by CH_2CH_2COOH, $CH_2CH_2COOCH_2CH_3$, $CH_2CH_2CH_2COOCH_2CH_3$, $CH_2CH_2COOCH_3$ or $CH_2CH_2CH_2COOCH_3$, and are in particular tert-butyl, or C_1-C_4alkoxy, especially methoxy, and
compounds of the formulae (Ib) and (Ic) in which at least two of the substituents R_1, R_2, R_3 or R_4 and two of the substituents R_{100}, R_{200}, R_{300} or R_{400} are not hydrogen, preferably R_1 and R_3 and R_{100} and R_{300} are not hydrogen and, with particular preference, R_1 and R_3 independently of one another are COOH- or COO(C_1-C_{12}alkyl)-substituted or unsubstituted C_1-C_8alkyl or C_1-C_8alkoxy, and, with very particular preference, R_1, R_3, R_{100} and R_{300} independently of one another are C_1-C_4alkyl which is unsubstituted or substituted by COOH or COO(C_1-C_4alkyl), in particular by CH_2CH_2COOH, $CH_2CH_2COOCH_2CH_3$, $CH_2CH_2CH_2COOCH_2CH_3$, $CH_2CH_2COOCH_3$ or $CH_2CH_2CH_2COOCH_3$, and in particular are tert-butyl, or C_1-C_4alkoxy, especially methoxy.

Also found have been processes for preparing the compounds of the formula (I), and their use.

Alkyl, alkenyl or alkylene can be straight-chain or branched or can be interrupted by oxygen, nitrogen and/or sulfur atoms. C_1-C_{24}Alkyl is therefore, for example, with very particular preference, C_1-C_4alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, cyclobutyl, with particular preference C_1-C_6alkyl, which corresponds to the definition given for C_1-C_4alkyl, and additionally is n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, cyclopentyl, cyclohexyl, n-hexyl, and preferably C_1-C_8alkyl, which corresponds to the definition given for C_1-C_6alkyl, and additionally is n-octyl, 1,1',3,3'-tetramethylbutyl, 2-ethylhexyl, and in particular C_1-C_{12}alkyl, which corresponds to the definition given for C_1-C_8alkyl, and additionally is trimethylcyclohexyl, decyl, menthyl, thujyl, bornyl, 1-adamantyl, 2-adamantyl or dodecyl, and also C_1-C_{15}alkyl, which corresponds to the definition given for C_1-C_{12}alkyl, and additionally is pentadecyl or tetradecyl, and, furthermore, hexadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl or tetracosyl.

C_1-C_{24}Alkylene is therefore, for example, methylene, ethylene, n-propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene, cyclobutylene, n-pentylene, 2-pentylene, 3-pentylene, 2,2-dimethylpropylene, cyclopentylene, cyclohexylene, n-hexylene, n-octylene, 1,1,3,3-tetramethylbutylene, 2-ethylhexylene, nonylene, trimethylcyclohexylene, decylene, menthylene, thujylene, bornylene, 1-adamantylene, 2-adamantylene, dodecylene, tetradecylene, hexadecylene, heptadecylene, octadecylene, eicosylene, heneicosylene, docosylene or tetracosylene.

C_2-C_{24}Alkenyl is C_2-C_{24}alkyl and preferably C_2-C_{12}alkenyl which is mono- or polyunsaturated, it being possible, if desired, for two or more double bonds to be isolated or conjugated, for example vinyl, allyl, 2-propen-2-yl, 2-buten-1-yl, 3-buten-1-yl, 1,3-butadien-2-yl, 2-cyclobuten-1-yl, 2-penten-1-yl, 3-penten-2-yl, 2-methyl-1-buten-3-yl, 2-methyl-3-buten-2-yl, 3-methyl-2-buten-1-yl, 1,4-pentadien-3-yl, 2-cyclopenten-1-yl, 2-cyclohexen-1-yl, 3-cyclohexen-1-yl, 2,4-cyclohexadien-1-yl, 2,5-hexadien-2-yl, 1-*p*-menthen-8-yl, 4(10)-thujen-10-yl, 2-norbornen-1-yl, 2,5-norbornadien-1-yl, 7,7-dimethyl-2,4-norcaradien-3-yl or the various isomers of hexenyl, octenyl, nonenyl, decenyl or dodecenyl.

C_1-C_{24}Alkoxy is O–C_1-C_{24}alkyl, preferably C_1-C_6alkoxy and, with particular preference, O-C_1-C_4alkyl, the alkyl radicals being as defined above.

C_1-C_{24} Alkylthio is S–C_1-C_{24}alkyl, preferably C_1-C_6alkthio and, with particular preference, S—C_1-C_4alkyl, the alkyl radicals being as defined above.

C_1-C_5Acyl is, for example, -CO-methyl, -CO-ethyl, -CO-propyl, -CO-iso-propyl, -CO-sec-butyl, -CO-tert-butyl, -CO-n-butyl,-OCO-n-pentyl or -CO-sec-amyl, -CO-tert-amyl.

C_2-C_{24}Alkyl, or C_2-C_{12}alkyl, interrupted by an oxygen atom, O, nitrogen atom, N, sulfur atom, S, is, for example, C_4alkyl, such as especially –CH_2–CH_2–O–CH_2–CH_3, –CH_2–CH_2–NH–CH_2–CH_3, or –CH_2–CH_2–S–CH_2–CH_3. C_2-C_{12}Alkyl doubly interrupted by O, N or S is for example C_6alkyl, such as especially –CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_3, –CH_2–CH_2–NH–CH_2–CH_2–NH–CH_2–CH_3, –CH_2–CH_2–S–CH_2–CH_2–S–CH_2–CH_3. O- and N-interrupted C_2-C_{12}alkyl is for example C_6alkyl, such as especially –CH_2–CH_2–O–CH_2–CH_2–NH–CH_2–CH_3. Oxo-substituted C_2-C_{12}alkyl is for example C_2alkyl, such as especially –C(=O)–CH_3. Oxo-substituted and O-interrupted C_2-C_{12}alkyl is for example C_8alkyl, such as especially -$(CH_2)_3$–O–C(=O)–$C(CH_3)_3$, –C(=O)–$(CH_2)_6$–OCH_3 or –$C(CH_3)_2$–COO–$(CH_2)_3$–CH_3.

C_2-C_{24}Alkylene interrupted by an oxygen radical, O, nitrogen radical, N, sulfur radical, S; is for example C_4alkylene, such as especially –CH_2–CH_2–O–CH_2–CH_2-, –CH_2–CH_2–NH–CH_2–CH_2-, or –CH_2–CH_2–S–CH_2–CH_2-. C_2-C_{24}Alkylene doubly interrupted by O, N or S is for example C_6alkylene, such as especially –CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2-, –CH_2–CH_2–NH–CH_2–CH_2–NH–CH_2–CH_2-, –CH_2–CH_2–S–CH_2–CH_2–S–CH_2–CH_2-. O- and N-interrupted C_2-C_{12}alkylene is for example C_6alkyl, such as especially –CH_2–CH_2–O–CH_2–CH_2–NH–CH_2–CH_2-. Oxo-substituted C_2-C_{24}alkylene is for example C_2alkylene, such as especially -C(=O)-CH_2-. Oxo-substituted and O-interrupted C_1-C_{24}alkylene is for example C_8alkylene, such as especially –$(CH_2)_3$–O–C(=O)–$C(CH_3)_2$-, –C(=O)–$(CH_2)_6$–OCH_2- or -$C(CH_3)_2$–COO–

$(CH_2)_3$–CH_2-. Single or multiple substitution by halogen, hydroxyl, oxo or cyano, and single or multiple interruption by O, S or N, generally alter only slightly the chemical reactivity of an alkyl, alkenyl or alkylenyl group.

C_5-C_{12}Cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, preferably C_5-C_6cycloalkyl such as cyclopentyl or cyclohexyl.

C_5-C_{12}Cycloalkylene is for example cyclopentylene, cyclohexylene, cycloheptylene, cyclooctylene or cyclododecylene such as 2-cyclopenten-1-yl, 2-cyclohexen-1-yl, 3-cyclohexen-1-yl, 2,4-cyclohexadien-1-yl or 1-*p*-menthen-8-yl, 4(10)-thujen-10-yl, 2-norbornen-1-yl, 2,5-norbornadien-1-yl, 7,7-dimethyl-2,4-norcaradien-3-yl, preferably C_5-C_6-cycloalkylene such as cyclopentylene or cyclohexylene.

Cycloalkyl or cycloalkylene can also be interrupted by heteroatoms such as, for example, -NH-, -S-, -O- or by units such as -CO-, -$CONH_2$, -CONH, -NH_2CO-, -COO- or -OCO-, and is for example piperazinyl or piperazinylene, phthalimide, piperazine-2,5-dienylene, tetrahydrofuryl, tetrahydropyryl, 2-pyrrolidonyl, thiolanyl, oxazolanyl, tetrahydroimidazolyl, tetrahydrothiazolyl, piperidinyl, dioxanyl.

C_5-C_{12}Cycloalkoxy is O–C_5-C_{12}cycloalkyl, preferably C_5-C_6cycloalkyl, the cycloalkyl radicals being as defined above.

C_5-C_{12}Cycloalkylthio is S–C_5-C_{12}cycloalkyl, preferably C_5-C_6cycloalkyl, the cycloalkyl radicals being as defined above.

Divalent polycyclic radicals are for example naphthyl, anthranyl or anthranylfuranoyl radicals.

A polycycle which can be interrupted by heteroatoms such as O, N, S or P is for example an aromatic, aliphatic or aromatic and aliphatic polycycle such as polyethers, for example a crown ether, and also polyamines or polythioethers, or for example octahydroquinolizine or tetradecahydroacridine.

Aralkyl and aryl is preferably C_7-C_{12}aralkyl or C_6-C_{12}aryl.

C_7-C_{25}Aralkyl is for example benzyl, 2-benzyl-2-propyl, β-phenylethyl, α,α-dimethylbenzyl, ω-phenylbutyl, ω,ω-dimethyl-ω-phenylbutyl, ω-phenyldodecyl, ω-phenyloctadecyl, ω-phenyleicosyl or ω-phenyldocosyl, preferably C_7-C_{18}aralkyl such as benzyl, 2-benzyl-

2-propyl, β-phenylethyl, α,α-dimethylbenzyl, ω-phenylbutyl, ω,ω-dimethyl-ω-phenylbutyl, ω-phenyldodecyl or ω-phenyloctadecyl, and with particular preference C_7-C_{12}aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenylethyl, α,α-dimethylbenzyl, ω-phenylbutyl, ω,ω-dimethyl-ω-phenylbutyl or ω-phenyldodecyl.

C_7-C_{12}Aralkyl is for example benzyl, 2-benzyl-2-propyl, β-phenylethyl, 9-fluorenyl, α,α-dimethylbenzyl, ω-phenylbutyl or ω,ω-dimethyl-ω-phenylbutyl.

C_6-C_{24}Aryl is for example phenyl, 1-naphthyl, 2-naphthyl, 4-biphenylyl, phenanthryl, 2- or 9-fluorenyl, anthraquinonyl or anthracenyl, preferably C_6-C_{12}aryl such as phenyl, 1-naphthyl, 2-naphthyl, 4-biphenylyl.

C_6-C_{12}aryl is for example phenyl, 1-naphthyl, 2-naphthyl, 4-biphenylyl or 2-fluorenyl.

C_6-C_{24}Aryloxy is O–C_6-C_{24}aryl, preferably C_6-C_{12}aryl, the aryl radicals being as defined above.

C_6-C_{24}Arylthio is S–C_6-C_{24}aryl, preferably C_6-C_{12}aryl, the aryl radicals being as defined above.

C_6-C_{24}Arylene is for example phenylene, 1-naphthylene, 2-naphthylene, 4-biphenylene, phenanthrylene, 2- or 9-fluorenylene, anthraquinonylene or anthracenylene, preferably C_6-C_{12}arylene such as phenylene, 1-naphthylene, 2-naphthylene or 4-biphenylene.

Bi(C_6-C_{24})arylene is preferably biphenylene, especially 1,4- or 1,3-biphenylenes.

5- or 6-membered heterocyclic ring is A_5-A_6heteroaryl or C_5-C_6cycloalkyl or C_5-C_6cycloalkylene interrupted by heteroatoms such as O, S, N.

A_5-A_{18}Heteroaryl is a polyunsaturated heterocyclic structure, preferably a monocyclic structure, such as preferably A_5-A_6heteroaryl, and bicyclic heteroaromatic radical, and is a heteroaromatic structure comprising 5 to 18 atoms, selected from C, N, O and S, which includes at least 6 conjugated π electrons. Heteroaryl is for example thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, benzimidazolyl, benzothiazolyl, dibenzofuranyl, phenoxythiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, quinolyl, isoquinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, carbolinyl, benzotriazolyl, benzoxazolyl,

phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl.

A_5-A_{18}Heteroaryloxy is O-A_5-A_{18}heteroaryl, the heteroaryl radicals being as defined above.

A_5-A_{18}Heteroarylthio is S-A_5-A_{18}heteroaryl, the heteroaryl radicals being as defined above.

A_5-A_{18}Heteroarylene is a polyunsaturated heterocyclic structure, preferably a monocyclic structure, such as preferably A_5-A_6heteroarylene, and bicyclic heteroaromatic radical, and is a heteroaromatic structure comprising 5 to 18 atoms, selected from C, N, O and S, which includes at least 6 conjugated π electrons. Heteroarylene is thienylene, benzo[b]thienylene, dibenzo[b,d]thienylene, thianthrenylene, furylene, furfurylene, 2H-pyranylene, benzofuranylene, isobenzofuranylene, dibenzofuranylene, phenoxythinylene, pyrrolylene, imidazolylene, pyrazolylene, pyridylene, bipyridylene, benzimidazolylene, benzothiazolylene, triazinylene, pyrimidinylene, pyrazinylene, pyridazinylene, indolizinylene, isoindolylene, indolylene, indazolylene, purinylene, quinolizinylene, quinolylene, isoquinolylene, phthalazinylene, naphthyridinylene, quinoxalinylene, quinazolinylene, cinnolinylene, pteridinylene, carbazolylene, carbolinylene, benzotriazolylene, benzoxazolylene, phenanthridinylene, acridinylene, perimidinylene, phenanthrolinylene, phenazinylene, isothiazolylene, phenothiazinylene, isoxazolylene, furazanylene or phenoxazinylene.

Bi(A_5-A_{18})heteroarylene is for example bipyridylene, bipyrrolylen, piperazinedionylen, quinodimethylene, imidazolonylen, isoindolinylen, and anthraquinoylfuranoylen, preferably bi(A_5-A_{10})heteroarylene and, with particular preference, piperazinedionylen and isoindolinylen.

Radical in primary or secondary amine radical is hydrogen or in hydrazone or amide radical is substituted or unsubstituted C_1-C_{24}alkyl, -CO-(C_1-C_{24}alkyl), -CO-O-(C_1-C_{24}alkyl), -CO-O-(C_6-C_{24}aryl), -CO-(C_6-C_{24}aryl), C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, a primary or secondary amine radical, C_6-C_{24}aryl, C_6-C_{24}aryloxy, C_6-C_{12}arylthio, C_7-C_{25}aralkyl or A_5-A_{18}heteroaryl.

Halogen is chlorine, bromine, fluorine or iodine, preferably fluorine or chlorine.

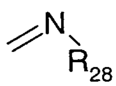
C_2-C_{12}alkyl or C_2-C_{12}alkenyl substituted one or more times by halogen, hydroxyl, C_1-C_{12}alkoxy or cyano is for example 2-chloroethyl, trifluoromethyl, pentafluoroethyl, β,β,β-trifluoroethyl, trichlorovinyl, ω-chloropropyl, ω-bromobutyl, perfluorohexyl,

perfluorododecyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, 2,3-dihydroxypropyl, 2,3-dimethoxypropyl, 2,3-dimethoxypropyl or 2-cyanoethyl, preferably trifluoromethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl or 2-cyanoethyl.

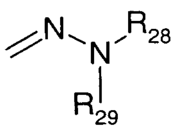
One particularly preferred embodiment of the present invention comprises compounds of the formulae (Ia), (Ib) or (Ic)

in which

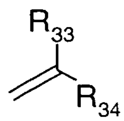
X_1 is a compound selected from the group of the compounds of the formulae (III), (IV), (VI) and (VIII)



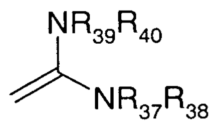
(III)



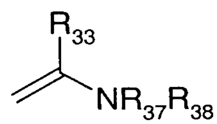
(IV)



(VI)



(VIII)



(VIIIa)

in which

R_{28}, R_{29}, R_{37}, R_{38}, R_{39} and R_{40} independently of one another are hydrogen or substituted or unsubstituted C_1-C_{24}alkyl, C_1-C_{24}alkoxy, C_5-C_{12}cycloalkoxy, C_5-C_{12}-cycloalkylthio, C_5-C_6cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_5-C_{24}aryloxy, C_5-C_{24}arylthio, C_7-C_{25}aralkyl, a primary or secondary amine radical, A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy, A_5-A_{18}heteroarylthio, and with particular preference are C_6-C_{12}aryl, C_7-C_{13}aralkyl, a primary or secondary amine radical, or A_5-A_8heteroaryl, with the proviso that R_{28} is not phenyl or 4-dimethylaminophenyl if R_1, R_2, R_3 and R_4 are hydrogen, or compound of the formula (IV) is excluded if R_1, R_2, R_3 and R_4 is hydrogen or one R_1, R_2, R_3 and R_4 is methyl,

and

R_{33} and R_{34} independently of one another correspond to the definition of R_{28}, with the proviso that R_{33} and R_{34} are not phenyl or

R_{33} is not hydrogen and R_{34} is not methyl, 4-aminophenyl, 4-dimethylaminophenyl or -OCO-4-(1-chlorophenylene) if R_1, R_2, R_3 and R_4 are hydrogen,

or R_{33} is not hydrogen and R_{34} is not 4-aminophenyl if R_1 and R_3 are tert-C_5H_{11}alkyl, or R_{33} is not hydrogen and R_{34} is not 2-hydroxyphenyl if R_1 and R_3 are tert-butyl, or R_{33} is not hydrogen and R_{34} is not a primary or secondary amine radical if R_3 is hydrogen, methoxy

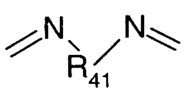
or hydroxyl and R_1, R_2 and R_4 are hydrogen, or

R_{33} is not hydrogen and R_{34} is not a secondary amine radical if R_1, R_2, R_3 and R_4 are hydrogen,

or

R_{33} and R_{34} together are a lactam, quinomethylene, hydantoin, acenaphthenequinone, azlactone, pyrazolonyl, barbituric acid, isoindolinone or isoindoline radical, and

X_2 is a compound selected from the group of compounds of the formulae (IX), (X), (XI), (XII) and (XIV),



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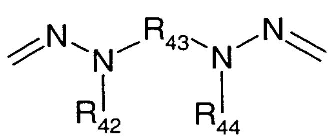
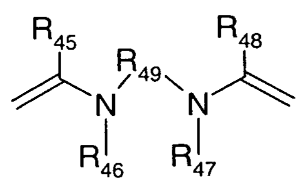
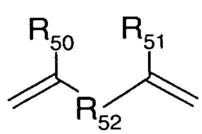


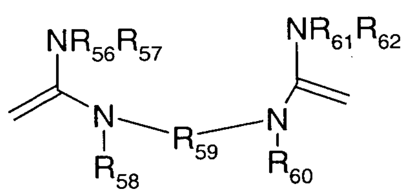
(X)



(XI)



(XII)



(XIV)

in which

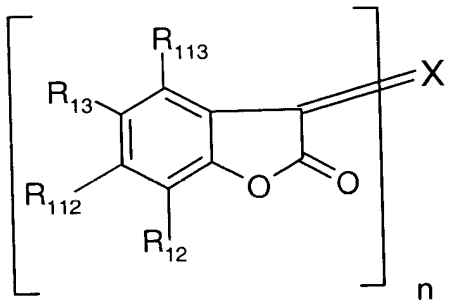
R_{42}, R_{44}, R_{46}, R_{47}, R_{50}, R_{51}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} independently of one another are hydrogen or substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24} alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl, divalent polyether, polyimine, polyamine radical, bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -NR_{42}CO-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-,
in which
R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl or A_5-A_{18}heteroaryl,

and with particular preference are C_1-C_{24}alkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl or A_5-A_8heteroaryl, and

R_{45} and R_{48} independently of one another are hydrogen, C_1-C_{24}alkyl, C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, C_5-C_{24}aryl, C_7-C_{25}aralkyl, C_5-C_{24}aryloxy, C_5-C_{24}arylthio or A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy, A_5-A_{18}heteroarylthio, and

R_{41}, R_{43}, R_{52}, R_{49} and R_{59} independently of one another are a direct bond or substituted or unsubstituted C_6-C_{24}arylene, A_5-A_{18}heteroarylene, C_5-C_{12}cycloalkylene or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -NR_{42}CO-, -CONR $_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-, in which
in which
R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl.

A further preferred embodiment of the present invention comprises compounds of the formula (XVI)



(XVI)

in which
n is 1 or 2, and
if n is 1
X is X_1, and corresponds to the above definition of X_1, and
if n is 2
X is X_2, and corresponds to the above definition of X_2, and

R_{12}, R_{112}, R_{13} and R_{113} independently of one another are hydrogen, halogen, OH, NO_2, R_{14},

OR_{14}, OC_9-C_{18}alkyl or SC_9-C_{18}alkyl,

in which

R_{14} is C_1-C_{24}alkyl which is unsubstituted or substituted one or more times by oxo or by $COO^- X_5^+$ and which can be uninterrupted or interrupted one or more times by O, N and/or S, or is C_7-C_{18}aralkyl or C_6-C_{12}aryl unsubstituted or substituted one or more times by halogen, OR_{16}, $NR_{16}R_{17}$, $COOR_{16}$, $CONR_{16}R_{17}$, $NR_{18}COR_{16}$ or $NR_{18}COOR_{16}$,

X_5^+ is a cation H^+, Na^+, K^+, $Mg^{++}{}_{1/2}$, $Ca^{++}{}_{1/2}$, $Zn^{++}{}_{1/2}$, $Al^{+++}{}_{1/3}$, or $[NR_{16}R_{17}R_{18}R_{19}]^+$, and

R_{16} and R_{17} independently of one another are hydrogen, C_6-C_{12}aryl, C_7-C_{10}aralkyl, or C_1-C_8alkyl which is unsubstituted or substituted one or more times by halogen, hydroxyl or C_1-C_4alkoxy, or

R_{16} and R_{17} in $NR_{16}R_{17}$ or $CONR_{16}R_{17}$, together with the nitrogen atom connecting them, are pyrrolidine, piperidine, piperazine or morpholine each of which is unsubstituted or substituted from one to four times by C_1-C_4alkyl,

and R_{18} and R_{19} independently of one another are hydrogen, C_1-C_8alkyl, C_6-C_{10}aryl or C_6-C_{12}aralkyl,

R_{12} and R_{112}, R_{112} and R_{13}, R_{13} and R_{113} can also independently of one another each together be divalent substituted or unsubstituted radicals, such as polycyclic radicals, preferably naphthylene or 1,3-butadien-1,4-ylene or –CH=CH–NH–, the latter resulting in an additional fused-on 5- or 6-membered ring, preferably a phenylene ring.

Preferably, R_{12}, R_{112}, R_{13} and R_{113} or the above divalent substituted or unsubstituted radicals independently of one another are hydrogen, OH, OR_{22}, $COOR_{16}$, $CONR_7R_8$, chlorine, $COO^-X_6^+$, R_{22}, C_2H_5-COOH, C_2H_5-COO(C_1-C_{12}alkyl) or C_2H_5-COO(C_1-C_{12}alkyl) which can be uninterrupted or interrupted one or more times by O, N, S, and in which C_1-C_{12}alkyl can be interrupted, and with very particular preference are OH, chlorine, $COO^-X_6^+$, $COOR_{16}$ or $CONR_7R_8$

in which

R_{22} is substituted or unsubstituted C_6-C_{12}aryl, C_7-C_{12}aralkyl or is C_1-C_8alkyl which is unsubstituted or substituted one or more times by oxo, cyano, $COOR_{16}$ or $COO^- X_6^+$ and which can be uninterrupted or interrupted one or more times by O, N, S,

X_6^+ is H^+, an alkali metal cation such as Na^+, K^+ or an alkaline earth metal cation such as $Mg^{++}{}_{1/2}$, $Ca^{++}{}_{1/2}$, or cations from Group 12 of the IUPAC form of the Periodic Table such as $Zn^{++}{}_{1/2}$ or from Group 13 of the IUPAC form of the Periodic Table such as $Al^{+++}{}_{1/3}$, or an ammonium radical $[NR_{24}R_{25}R_{26}R_{27}]^+$, in which

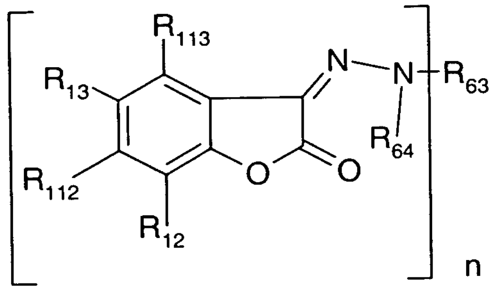
R_{24}, R_{25} and R_{26} independently of one another are C_1-C_4alkyl or phenyl, and

R_{27} is hydrogen, C_1-C_8alkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl,

Preferably, R_{12} and R_{13} and R_{112} and R_{113} are not hydrogen, and with particular preference independently of one another are tert-butyl, O-CH_3, CH_2CH_2COOH or $CH_2CH_2COO(C_1$-C_{12}alkyl), $CH_2CH_2CH_2COO(C_1$-C_{12}alkyl), and with very particular preference
R_{12} is tert-butyl and
R_{13} is tert-butyl, O-CH_3, CH_2CH_2COOH or $CH_2CH_2COO(C_1$-C_{12}alkyl), $CH_2CH_2CH_2COO(C_1$-C_{12}alkyl) and
R_{112} and R_{113} are hydrogen,
or
R_{113} is hydrogen or OH,
or
R_{12} together with R_{112} is a divalent fused-on phenylene radical and
R_{13} and R_{113} are hydrogen,
or
R_{13} together with R_{113} is a divalent fused-on phenylene radical and R_{12} and R_{112} are hydrogen.

Further in particular, with very particular preference,
R_{12} is tert-butyl and
R_{13} is tert-butyl, O-CH_3, CH_2CH_2COOH or $CH_2CH_2COOCH_2CH_3$, $CH_2CH_2CH_2COOCH_2CH_3$, $CH_2CH_2COOCH_3$, $CH_2CH_2CH_2COOCH_3$, and
R_{112} is Hydrogen.

One particularly preferred embodiment of the present invention comprises compounds of the formulae (Ia), (Ib) or (Ic) in which X_1 is a hydrogen radical of the formula (IV) and X_2 is a compound of the formulae (X), especially =N-$NR_{63}R_{64}$, and with very particular preference is a compound of the formula (XVII)



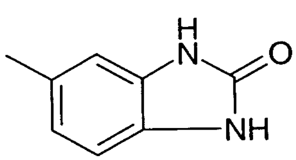
(XVII)

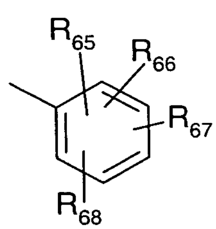
in which

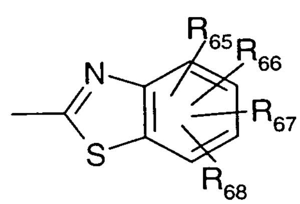
if n is 1

R_{64} independently of R_{63} is a radical as defined under R_{63} or hydrogen, and

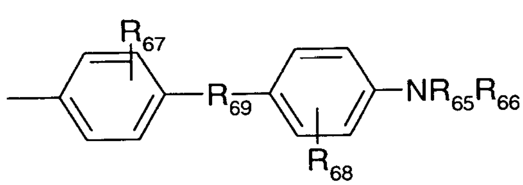
R_{63} is substituted or unsubstituted C_1-C_{12}alkyl, C_5-C_{12}cycloalkyl, C_2-C_6alkenyl, C_6-C_{12}aryl, C_7-C_{13}aralkyl, or A_5-A_{12}heteroaryl, especially anthranyl, and with particular preference is C_6-C_{12}aryl, C_7-C_{12}aralkyl or A_5-A_8heteroaryl, and with very particular preference is a compound selected from the group of the compounds of the formulae (XVIII), (IXX), (XX) and (XXI),







(XVIII) (IXX) (XX)



(XXI)

in which

R_{65} and R_{66} independently of one another are hydrogen, hydroxyl, cyano, nitro, halogen, especially fluoro or chloro, are C_5-C_6cycloalkyl, unsubstituted or R_{67}-substituted phenyl or are C_1-C_{18}alkyl, C_1-C_{18}alkoxy, in which alkyl especially is methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, sec-amyl, tert-amyl, hexyl or 2,2-dimethylbutyl, and

R_{68} independently of R_{67} has the same definition as R_{67}, and

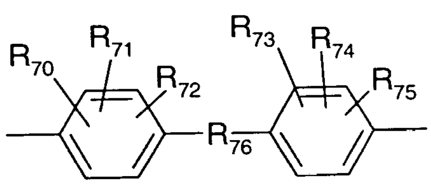
R_{69} is a direct bond $-CH_2-$, $-CH(CH_3)-$, $-C(CH_3)_2-$, $-CH=N-$, $-N=N-$, $-O-$, $S-$, $-SO-$, $-SO_2-$ or $-NR_{65}-$,

R_{67} is hydrogen, nitro, cyano, halogen such as fluorine, chlorine, bromine, iodine or C_1-C_8-alkyl, C_1-C_6alkoxy, unsubstituted or $NR_{65}R_{66}$-substituted C_5-C_6cycloalkyl, and is preferably nitro, chlorine, C_1-C_6alkyl or C_1-C_6alkoxy,

with the proviso that, if R_1, R_2, R_3 and R_4 are hydrogen or one R_1, R_2, R_3 or R_4 is methyl, the hydrazone radical is excluded, and

if n is 2

R_{63} is unsubstituted or substituted C_6-C_{18}arylene, A_5-A_{18}heteroarylene, C_5-C_6cycloalkyl or a divalent polymethylidene, polyether, polyimine, polyamine radical, or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be attached to one another and/or interrupted by one or more intermediate units such as $-CH=CH-$, $-CH=N-$, $-N=N-$, $-CR_{44}R_{42}-$, $-CO-$, $-COO-$, $-OCO-$, $-NR_{42}CO-$, $-CONR_{42}-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$ or $-NR_{42}-$, and with particular preference is a compound selected from the group of compounds of the formulae (XXII) and (XXIII)



(XXII) and $-((CH=CH)_{m1}-Y1)_r-(CH=CH)_{m2}-$ (XXIII)

in which

R_{70}, R_{71}, R_{72}, R_{73}, R_{74} and R_{75} independently of one another correspond to the definition of R_{65}, and with particular preference at least two R_{70}, R_{71}, R_{72}, R_{73}, R_{74} or R_{75} independently of one another are hydrogen, and

R_{76} is a direct bond or is one or more $-CH=N-$, $-N=N-$, $-CR_{45}R_{48}-$, $-CO-$, $-COO-$, $-OCO-$, $-NR_{46}CO-$, $-CONR_{46}-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$ or $-NR_{46}-$ units and with very particular preference is a direct bond, and,

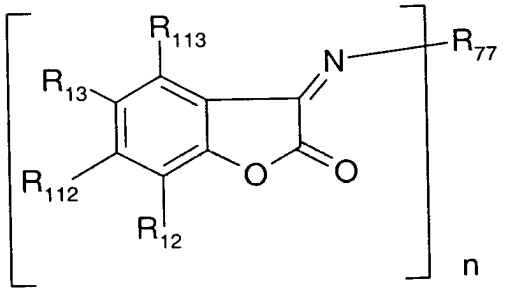
with especial particular preference, in which R_{76} is a direct bond and R_{70}, R_{71}, R_{72}, R_{73}, R_{74} and R_{75} independently of one another are chlorine or hydrogen,

Y1 is a direct bond or C_6-C_{18}arylene, such as substituted or unsubstituted phenylene, especially 1,4-phenylene which is unsubstituted or substituted one or more times by halogen, nitro, cyano or amine, or is A_5-A_{18}heteroarylene, C_5-C_{12}cycloalkyl, such as in particular cyclohexylene or piperazinylene, or bi(C_6-C_{18})arylene, especially unsubstituted or substituted biphenylene, or bi(A_5-A_{18})heteroarylene, or is -CH=N-, -N=N-, -$CR_{74}R_{75}$-, -CO-, -COO-, -OCO-, -NR_{65}CO-, -$CONR_{65}$-, -O-, -S-, -SO-, -SO_2- or -NR_{65}- units, and

r is an integer from 0 to 10, and preferably is 0, 1 or 2,

m1 and m2 is an integer from 0 to 10, and preferably is 0, 1 or 2, and with particular preference r and m2 are not zero.

A further particularly preferred embodiment of the present invention comprises compounds of the formula (Ia), (Ib) or (Ic) in which X_1 is an imine radical of the formula (III) and X_2 is a compound of the formula (IX), especially = N-R_{77} and, with very particular preference, is a compound of the formula (XXIV)



(XXIV)

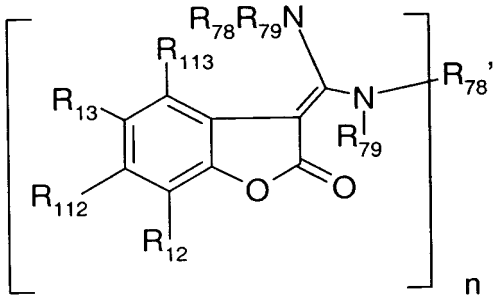
in which, if n is 1,

R_{77} is substituted or unsubstituted C_1-C_{12}alkyl, C_5-C_6cycloalkyl, C_2-C_6alkenyl, C_6-C_{12}aryl, C_7-C_{13}aralkyl, or A_5-A_{12}heteroaryl, and

with very particular preference is a compound of the formula (IXX), especially with very particular preference is a compound of the formula (IXX) in which R_{65}, R_{66}, R_{67} or R_{68} independently of one another are hydroxyl or hydrogen, with the proviso that in formula

(XXIV), if R_{12}, R_{112}, R_{13} or R_{113} are hydrogen, R_{77} is not unsubstituted phenylimine- or 4-dimethylaminephenylimine.

Furthermore, the present invention provides with particular preference compounds of the formula (Ia), (Ib) or (Ic) in which X_1 is a compound of the formula (VIII) and X_2 is a compound of the formula (XI) or (XIV), in particular a compound of the formula (XXV)



(XXV)

in which,

if n is 1,

R_{78}, R_{78}' and R_{79} independently of one another are hydrogen or substituted or unsubstituted C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_{12}alkylthio, C_5-C_6cycloalkoxy, C_5-C_6cycloalkylthio, C_6-C_{24}aryloxy, C_6-C_{24}arylthio or A_5-A_{12}heteroaryloxy, A_5-A_{12}heteroarylthio, C_5-C_6cycloalkyl, C_2-C_{12}alkenyl, C_6-C_{12}aryl, C_7-C_{13}aralkyl, or A_5-A_{12}heteroaryl or dependently of one another are hydrogen, and, with very particular preference, independently of one another are a compound of the formula (IXX) or hydrogen,

and

if n is 2

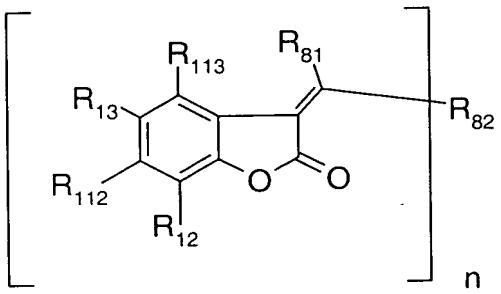
R_{78} and R_{79} correspond to the above definition if n is 1, and

$R_{78'}$ is a direct bond or substituted or unsubstituted C_6-C_{24}arylene, A_5-A_{18}heteroarylene, C_5-C_{12}cycloalkyl or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -NR_{42}CO-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-,

in which

R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl.

The present invention further provides, in one particularly preferred embodiment, compounds of the formula (Ia), (Ib) or (Ic), in which X_1 is a compound of the formula (VI) or (VII) and X_2 is a compound of the formula (XII), in particular and with very particular preference is a compound of the formula (XXVI)



(XXVI)

in which,

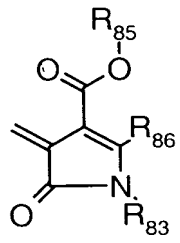
if n is 1,

R_{81} and R_{82} are C_6-C_{12}aryl if R_{12}, R_{112}, R_{13} or R_{113} are not hydrogen, or,

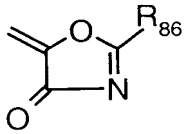
R_{81} and R_{82} independently of one another are hydrogen or unsubstituted or substituted C_1-C_{12}alkyl, -CO-(C_1-C_{24}alkyl), -CO-O-(C_1-C_{24}alkyl), C_6-C_{12}aryloxy, C_1-C_{12}alkoxy, C_1-C_{12}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_2-C_{12}alkenyl, a primary or secondary amine radical, C_6-C_{18}aryl, with particular preference are anthranyl, substituted or unsubstituted phenyl, C_5-C_{12}cycloalkyl, A_5-A_{12}heteroaryl such as benzimidazolyl or benzothiazolyl, or are -CO-O-(C_6-C_{24}aryl), -CO-(C_6-C_{24}aryl), C_6-C_{18}aryloxy, C_6-C_{18}arylthio or A_5-A_{12}heteroaryl, A_5-A_{12}heteroaryloxy, A_5-A_{12}heteroarylthio, and with particular preference are C_5-C_{12}aryloxy, C_1-C_6alkoxy, C_5-C_6cycloalkoxy,

or

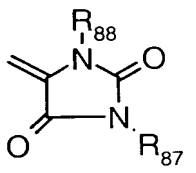
R_{81} and R_{82} together are a lactam, quinomethylene, hydantoin, acenaphthenequinone, azlactone, pyrazolonyl, barbituric acid, isoindolinone or isoindoline radical, of the formulae (XXVII, XXVIIa-XXVIId), (XXVIII), (IXXX, IXXXa-IXXXc) or (IXC).



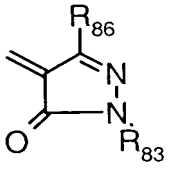
(XXVII)



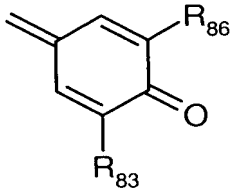
(XXVIIa)



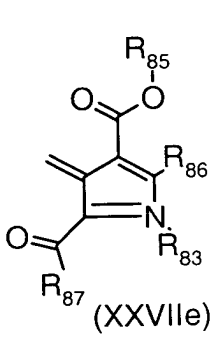
(XXVIIb)

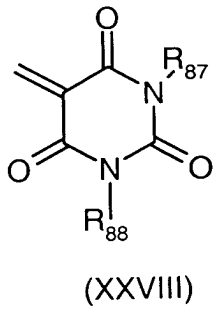


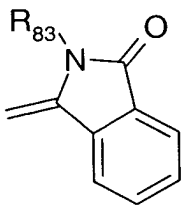
(XXVIIc)

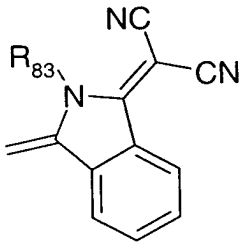


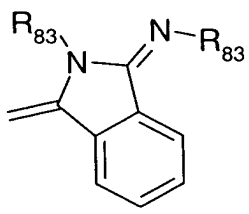
(XXVIId)

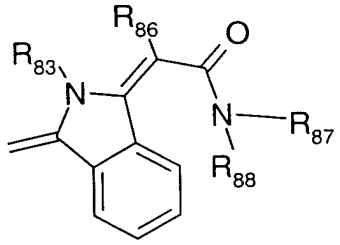

(XXVIIe)

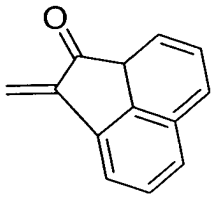

(XXVIII)


(IXXXa)


(IXXXb)


(IXXXc)


(IXXX)


(IXC)

with particular preference are a compound of the formula (XXVIII), (IXC), (IXXX), (IXXXb), (IXXXa) or (XXVIIa),

in which

R_{83}, R_{85}, R_{87} and R_{88} independently of one another are substituted or unsubstituted C_1-C_{18}alkyl, -CO-(C_1-C_{24}alkyl), -CO-O-(C_1-C_{24}alkyl), C_5-C_{12}cycloalkyl, C_2-C_{18} alkenyl, C_6-C_{18}aryl, -CO-O-(C_6-C_{24}aryl), -CO-(C_6-C_{24}aryl), C_7-C_{19}aralkyl or A_5-A_{18}heteroaryl, and with particular preference are C_6-C_{12}aryl, C_7-C_{13}aralkyl or A_5-A_8heteroaryl, and

R_{86} is hydrogen or substituted or unsubstituted C_1-C_{18}alkyl, C_1-C_{18} alkoxy, C_1-C_{18} alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{18}alkenyl, C_6-C_{18}aryl or C_7-C_{19}aralkyl,

with the proviso that $R_{81}$and R_{82} are not phenyl or
R_{81} is not hydrogen and R_{82} is not methyl, 4-aminophenyl, 4-dimethylaminophenyl or -OCO-4-(1-chlorophenylene) if R_1, R_2, R_3 and R_4 are hydrogen, or
R_{81} is not hydrogen and R_{82} is not 4-aminophenyl if R_1 and R_3 are tert-C_5H_{11}alkyl, or R_{81} is not hydrogen and R_{82} is not 2-hydroxyphenyl if R_1 and R_3 are tert-butyl, or
R_{81} is not hydrogen and R_{82} is not a primary or secondary amine radical, if R_3 is hydrogen, methoxy or hydroxyl and R_1, R_2 and R_4 are hydrogen, or
R_{81} is not hydrogen and R_{82} is not a secondary amine radical, if R_1, R_2, R_3 and R_4 are hydrogen, and

if n is 2

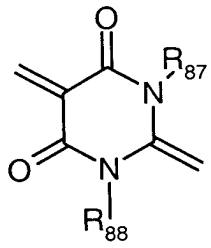
R_{82} is a single bond, an unsubstituted or substituted C_6-C_{18}arylene, especially 1,2-phenylene, 1,3-phenylene, 1,4-phenylene or naphthylene or (A_5-A_{18})heteroarylene or bi(C_6-C_{24})arylene, especially biphenylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene or C_2-C_{24}alkenylene, can be interrupted by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -$NR_{42}CO$-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-,

in which

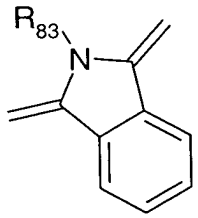
R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24} alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl,

or

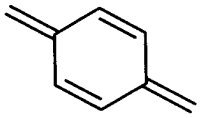
R_{81} and R_{82} together are a divalent unsubstituted or substituted (A_5-A_{18})heteroarylene or (C_6-C_{24})arylene radical, and with particular preference are a radical of the formula (CX), (CXI), (CXII) or (CXIII)



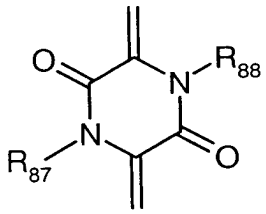
(CX)



(CXI)



(CXII)



(CXIII)

and with very particular preference are (CXI).

With particular preference, R_{82}, if n is 2, is unsubstituted or mono- or poly-halogen-, -nitro-, -hydroxyl-, -C_1-C_6alkyl-, -C_1-C_6alkoxy-substituted (A_5-A_{12})heteroarylene, 1,3-phenylene, 1,4-phenylene or bi(C_6-C_{24})arylene or bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene can be interrupted by a direct bond or one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-,-COO-, -OCO-, -$NR_{42}CO$-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-,

in which

R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl, and very particularly are 1,4-phenylene which is unsubstituted or substituted one or more

times by halogen, nitro, hydroxyl, C_1-C_6alkyl, C_1-C_6alkoxy.

With particular preference, furthermore, R_{81}, if n is 1, is NH_2 and R_{82} is substituted or unsubstituted phenyl.

Also very particularly preferred are compounds of the formula (XXVI) in which,

if n is 1

R_{81} is hydrogen and

R_{82} is -C_6H_5-R_{80}, -CH=CH-R_{80} or -R_{80}

in which

R_{80} is substituted or unsubstituted C_1-C_{24}alkyl, C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, C_6-C_{24}aryloxy, C_6-C_{24}arylthio, A_5-A_{18}heteroaryl, A_5-A_{18}heteroaryloxy or A_5-A_{18}heteroarylthio, especially C_6-C_{24}aryl or A_5-A_{18}heteroaryl, with particular preference for furyl, or substituted or unsubstituted phenyl or naphthyl, the substituents being preferably hydroxyl, methyl, dimethylamine, diphenylamine or methoxy, and,

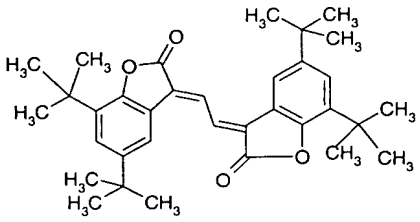
if n is 2,

R_{81} is hydrogen and

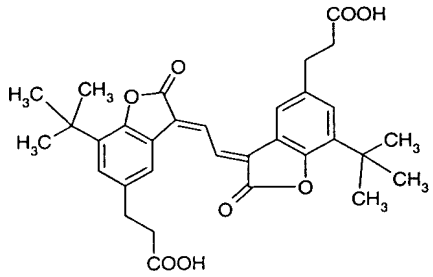
R_{82} is -CH=Q_1, -CH=Q_2, -C_6H_5-CH=Q_1 or -C_6H_5-CH=Q_2, and, with very particular preference, in which at least two of the substituents R_1, R_2, R_3 or R_4 are not hydrogen, preferably R_1 and R_3 are not hydrogen and, with particular preference, R_1 and R_3 independently of one another are COOH- or COO(C_1-C_{12}alkyl)-substituted or unsubstituted C_1-C_8alkyl or C_1-C_8alkoxy, and, with very particular preference, R_1 and R_3 independently of one another are C_1-C_4alkyl which is unsubstituted or substituted by COOH or COO(C_1-C_4alkyl), in particular by CH_2CH_2COOH, $CH_2CH_2COOCH_2CH_3$, $CH_2CH_2CH_2COOCH_2CH_3$, $CH_2CH_2COOCH_3$ or $CH_2CH_2CH_2COOCH_3$ especially tert-butyl, or C_1-C_4alkoxy, especially methoxy, and

compounds of the formulae (Ib) and (Ic) in which at least two of the substituents R_1, R_2, R_3 or R_4 and two of the substituents R_{100}, R_{200}, R_{300} or R_{400} are not hydrogen, preferably R_1 and R_3 and R_{100} and R_{300} are not hydrogen and, with particular preference, R_1 and R_3 independently of one another are COOH- or COO(C_1-C_{12}alkyl)-substituted or unsubstituted C_1-C_8alkyl or C_1-C_8alkoxy, and, with very particular preference, R_1 and R_3 and R_{100} and R_{300} independently of one another are C_1-C_4alkyl which is unsubstituted or substituted by COOH or COO(C_1-C_4alkyl), in particular by CH_2CH_2COOH, $CH_2CH_2COOCH_2CH_3$, $CH_2CH_2CH_2COOCH_2CH_3$, $CH_2CH_2COOCH_3$ or $CH_2CH_2CH_2COOCH_3$, especially tert-butyl, or C_1-C_4alkoxy, especially methoxy.

Furthermore, very particular preference is given to the compounds of the formula (XCa) or (XCb)



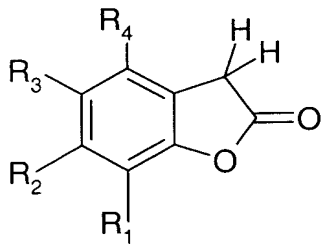
(XCa)



(XCb)

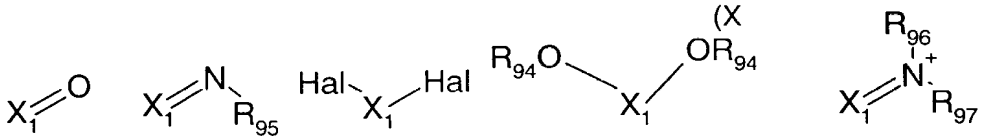
The compounds of the formula (I) according to the invention are generally obtained by C-H-acidic coupling reaction of a benzofuran-2-one with a couplable compound in the presence of an acidic or basic catalyst (in analogy to Organikum, 19th Edition 1993, pp. 459-495).

Accordingly, the present invention likewise provides a process for preparing the benzofuran-2-ones (Ia) by reacting benzofuran-2-one (XXXa)



(XXXa)

with a compound of the formula (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa)



XXXIa XXXIIa XXXIIIa XXXIVa XXXVa

in which

Hal is halogen, and

R_{94} has the same definition as R_{36}, and

R_{95} is hydrogen and hydroxyl,

R_{96} and R_{97} independently of one another are C_6-C_{12}aryl, especially phenyl, or are C_1-C_5acyl, C_6-C_{12}aralkyl, C_1-C_4alkyl, and R_{96} and R_{97} in particular are methyl, or phenyl and

CH_3CO, or phenyl and methyl, and
X_1 is X_7 and corresponds to the definition of X_1 with the exception of the hydrazone and imine radical.

The reaction is usually started by bringing benzofuran-2-one (XXXa) into contact with a compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa) in accordance with methods known per se, for example by mixing the starting materials or adding one starting material dropwise to the other.

The molar ratio of a compound (XXXa) to a compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa) is generally chosen in the range from 0.8:1 to 3:1; preferably, the molar ratio lies within the range from 0.9:1 to 2:1.

If desired, the reaction can be carried out in an organic solvent or in a melt; preferably, the reaction is carried out in an organic solvent.

The molar ratio of organic solvent to the compound (XXXa) is generally chosen in the range from 500:1 to 1:2, preferably from 100:1 to 1:1.

The reaction temperature is usually chosen in the range from -20 to 250°C, preferably from 0 to 200°C, the reaction temperature chosen preferably being a temperature at which the reaction mixture boils; it lies within the region of the boiling temperature of the solvent used.

The pressure chosen is preferably atmospheric pressure.

The reaction time is usually chosen as a function of the reactivity of the starting materials, and of the chosen temperature, and is generally within the range from 10 minutes to 48 hours.

If desired, the reaction can be carried out in the presence of a catalyst.

In general, the molar ratio of the catalyst to the compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa) is chosen in the range from 0.001:1 to 5:1, preferably in the range from 0.001:1 to 1:1.

Both acidic and basic catalysts are suitable.

Examples of acidic catalysts which can be used as inorganic acids, such as hydrochloric, phosphoric, hydrobromic or sulfuric acid, or zinc chloride, aluminium chloride or boron trifluoride, or organic acids or alkyl acids such as formic, acetic, propionic, chloroacetic or trifluoroacetic acid, or sulfonic acids such as arylsulfonic acids such as p-toluene- or methanesulfonic acid or silicates such as Fulkat 40 (Pontecchio Marconi), Katalysator K10 (Süd Chemie) or Katalysator Rudex (Rudex Nebelova Bratislava).

Examples of suitable basic catalysts are organic amines such as triethylamine, dialkylamine, piperidine, pyrrolidine, pyridine, morpholine, N,N-dimethylaniline, or aliphatic alkoxides, such as, for example, sodium methoxide, ethoxide, propoxide or butoxide or potassium tert-butoxide, or aromatic alkoxides such as phenoxide, for example, or carboxylic salts such as, for example, sodium or potassium acetate, or alkali metal or alkaline earth metal oxides, hydroxides, hydrides or carbonates, such as, for example, sodium or potassium hydroxide, sodium or potassium hydride, calcium oxide, magnesium oxide, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, or ammonia or tetrabutylammonium hydroxide.

As the solvent it is common to choose organic solvents, especially inert organic solvents, such as, for example, ethers such as tetrahydrofuran, dioxane, diethyl ether, methyl tert-butyl ether, glycols and their ethers such as, for example, mono-, di-, tri-, tetraethylene glycol, propylene glycol, the methyl, ethyl and butyl ethers thereof, or C_5-C_{12}alkanes such as pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane or C_5-C_{12}cycloalkane such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane or cyclododecane or, in particular, halogenated alkanes such as dichloromethane, dichloroethane, trichloromethane, tetrachloromethane, dichloroethylene, trichloroethane or tetrachloroethane, or aryls such as benzene, toluene, or xylene, chloro-, dichloro-, trichlorobenzene, or alcohols such as methanol, ethanol, propanol, sec-propanol, butanol, or carboxylic acids such as, for example, formic acid, acetic acid, propionic acid, or esters such as ethyl acetate, polar aprotic solvents such as N,N-dimethylformamide, N-methylpyrrolidine, dimethylacetamide or dimethyl sulfoxide.

Furthermore, the reaction is carried out, with particular preference, under an inert gas atmosphere. The inert gas used can comprise noble gases, preferably helium and argon, and also nitrogen.

It has been found advantageous in the process of the invention to use additions of binding agents such as anhydrides, especially acetic anhydride, or to use physical methods, such as distillation, for example, to remove leaving groups that are formed.

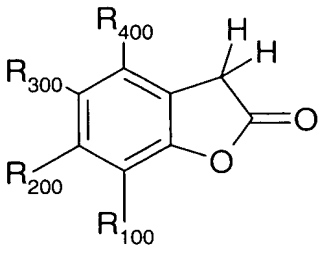
The molar ratio of anhydride to the compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa) lies within the range from 0.1:1 to 5:1, preferably in the range from 0.5:1 to 2:1.

The product can be isolated by the conventional methods, such as by filtration and, if desired, by subsequent washing of the filter residue with, for example, water and/or an organic solvent such as methanol, and drying of the moist filter residue.

Normally, the organic phase, for example, comprising the reaction product, is washed with water and subsequently concentrated, preferably to dryness. In a further variant of working up, the organic reaction product can also be concentrated by evaporation directly and then purified by means, for example, of recrystallization or column-chromatographic separation. In the case of recrystallization, isolation is normally done by filtration and subsequent washing of the filter residue with, preferably, a solvent in which the reaction product is poorly soluble. The column-chromatographed organic phase comprising the reaction product can be concentrated by evaporation directly. If desired, the reaction products can be dried after isolation. This is generally done using conventional drying apparatus such as drying ovens or paddle dryers.

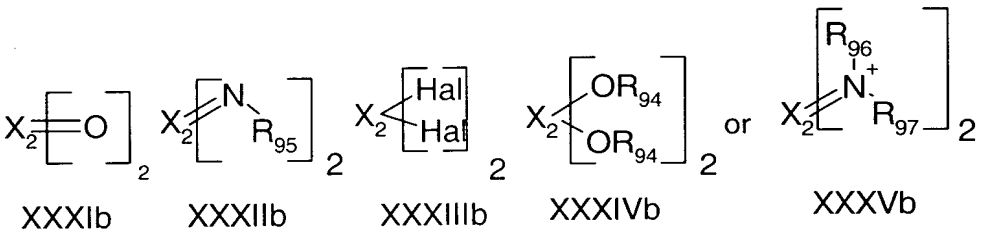
In the process of the invention it has been found advantageous to work up the product by adding, for example, water and/or acid and then subjecting the crude product to extraction with an organic solvent, such as toluene. In general, the organic phase, comprising the crude product, is washed with water and then concentrated by evaporation. If desired, the crude product is subsequently recrystallized. In general, for this purpose, the crude product is admixed with an organic solvent such as methanol, for example, and the resulting mixture is heated at boiling. Normally, the boiling temperature is maintained until all of the product has dissolved. Subsequently, the mixture is cooled, usually to a temperature in the range from -20 to 40°C, and filtered, the product being obtained as the filter residue. Normally, the filter residue is subsequently dried in vacuo in the range from 40 to 200°C, preferably in the range from 60 to 120°C.

In addition, the present invention also provides a process for preparing the benzofuran-2-ones (Ib) or (Ic) by reacting benzofuran-2-one (XXXa), or (XXXa) and a compound of the formula (XXXb)



(XXXb)

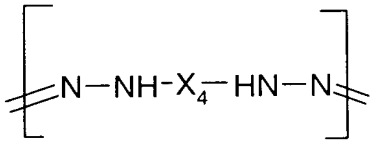
with a compound of the formulae (XXXIb), (XXXIIb), (XXXIIIb), (XXXIVb) or (XXXVb)



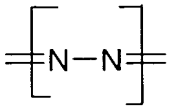
XXXIb XXXIIb XXXIIIb XXXIVb XXXVb

in which

X_2 is X_8 and corresponds to the definition of X_2, with the exception of X_2

being 

or



.

The reaction is normally started by bringing benzofuran-2-ones of the formula (XXXa) or (XXXa) and (XXXb) into contact with a compound of the formulae (XXXIb), (XXXIIb), (XXXIVb) or (XXXVb), in analogy to known methods, for example by mixing the starting components, or adding one starting component dropwise to the other, it being possible to react the benzofuran-2-ones (XXXa), or (XXXa) and (XXXb), in two portions or one portion.

In general, the molar ratio of a compound (XXXa), or (XXXa) and (XXXb), to a compound of the formulae (XXXIb), (XXXIIb), (XXXIIIb), (XXXIVb) or (XXXVb) is chosen in the range from 1:0.9 to 1:0.2; preferably, the molar ratio is situated within the range from 1:0.6 to 1:0.4.

If desired, the reaction can be carried out in an organic solvent or in a melt; preferably, the reaction is carried out in an organic solvent.

The molar ratio of organic solvent to the compound (XXXa), or (XXXa) and (XXXb), is generally chosen in the range from 500:1 to 1:2, preferably from 100:1 to 1:1.

The reaction temperature is usually chosen within the range from -20 to 250°C, preferably from 0 to 200°C; in general it has been found advantageous to choose as the reaction temperature a temperature at which the reaction mixture boils; it lies within the range of the boiling temperature of the solvent used.

The pressure chosen is preferably atmospheric pressure.

The reaction time is usually chosen as a function of the reactivity of the starting materials, and of the chosen temperature; it is generally situated within the range from 10 minutes to 48 hours.

If desired, the reaction can be carried out in the presence of a catalyst.

In general, the molar ratio of the catalyst to the compound of the formulae (XXXIb), XXXIIb), (XXXIIIb), (XXXIVb) or (XXXVb) is chosen in the range from 0.001:1 to 5:1, preferably in the range from 0.001:1 to 1:1.

Both acidic and basic catalysts are suitable.

Catalysts and solvents are as defined above.

Furthermore, the reaction is carried out, with particular preference, under an inert gas atmosphere. The inert gas used can comprise noble gases, preferably helium and argon, and also nitrogen.

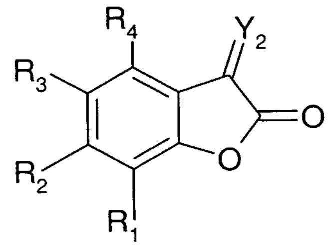
It has been found advantageous in the process of the invention to use additions of binding agents such as anhydrides, especially acetic anhydride, or to use physical methods, such as

distillation, for example, to remove leaving groups that are formed.

The molar ratio of anhydride to the compound of the formulae (XXXIb), (XXXIIb), (XXXIIIb), (XXXIVb) or (XXXVb) lies within the range from 0.1:1 to 5:1, preferably within the range from 0.5:1 to 2:1.

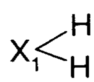
Working up and isolation are carried out as described above.

In addition, the present invention further provides a process for preparing the benzofuran-2-ones (Ia) by reacting 3-oxobenzofuran-2-one (XXXVIa)



(XXXVIa)

with a compound of the formula (XXXVIIa)



(XXXVIIa),

in which

Y_2 is O, NR_{95} or $N^+(R_{96}R_{97})$, NO or two chlorine atoms, the chlorine atoms each forming a single bond with the benzofuran-2-one (Ia).

The reaction is usually started by bringing 3-oxobenzofuran-2-one (XXXVIa) into contact with a compound of the formulae (XXXVIIa) in accordance with methods known per se, for example by mixing the starting materials or adding one starting material dropwise to the other.

The molar ratio of a compound (XXXVIa) to a compound of the formulae (XXXVIIa) is generally chosen in the range from 0.8:1 to 3:1; preferably, the molar ratio lies within the range from 0.9:1 to 2:1.

If desired, the reaction can be carried out in an organic solvent or in a melt; preferably, the reaction is carried out in an organic solvent.

The molar ratio of organic solvent to the compound (XXXVIa) is generally chosen in the range from 500:1 to 1:2, preferably from 100:1 to 1:1.

The reaction temperature is usually chosen in the range from -20 to 250°C, preferably from 0 to 200°C, the reaction temperature chosen preferably being a temperature at which the reaction mixture boils; it lies within the region of the boiling temperature of the solvent used.

The pressure chosen is preferably atmospheric pressure.

The reaction time is usually chosen as a function of the reactivity of the starting materials, and of the chosen temperature, and lies generally within the range from 10 minutes to 48 hours.

If desired, the reaction can be carried out in the presence of a catalyst.

In general, the molar ratio of the catalyst to the compound of the formulae (XXXVIIa) is chosen in the range from 0.001:1 to 5:1, preferably in the range from 0.001:1 to 1:1.

Both acidic and basic catalysts are suitable.

Catalysts and solvents are as defined above.

Furthermore, the reaction can, if desired, be carried out under an inert gas atmosphere. The inert gas used can comprise noble gases, preferably helium and argon, and also nitrogen.

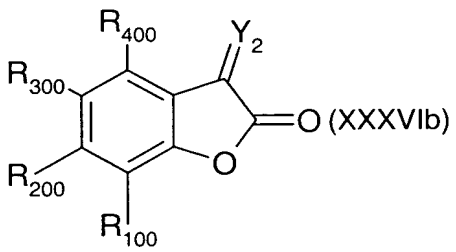
It has been found advantageous in the process of the invention to use additions of binding agents such as anhydrides, especially acetic anhydride, or to use physical methods, such as distillation, for example, to remove leaving groups that are formed.

The molar ratio of anhydride to the compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa) usually lies within the range from 0.1:1 to 5:1, preferably within the range from 0.5:1 to 2:1.

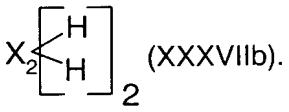
Working up and isolation are carried out as described above.

A further embodiment of the process of the invention comprises preparing the benzofuran-2-ones (Ib) or (Ic) by reacting 3-oxobenzofuran-2-one (XXXVIa), or (XXXVIa) and a

compound of the formula (XXXVIb)



with a compound of the formula (XXXVIIb)



The reaction is normally started by bringing 3-oxobenzofuran-2-ones of the formula (XXXVIa), or (XXXVIa) and (XXXVIb) into contact with a compound of the formula (XXXVIIb) in analogy to known methods, for example by mixing the starting components, or adding one starting component dropwise to the other, it being possible to react the 3-oxobenzofuran-2-ones (XXXVIa), or (XXXVIa) and (XXXVIb), in two portions or one portion.

In general, the molar ratio of a compound (XXXVIa), or (XXXVIa) and (XXXVIb), to a compound of the formulae (XXXVIIb) is chosen in the range from 1:0.9 to 1:0.2; preferably, the molar ratio lies within the range from 1:0.6 to 1:0.4.

If desired, the reaction can be carried out in an organic solvent or in a melt; preferably, the reaction is carried out in an organic solvent.

The molar ratio of organic solvent to the compound (XXXVIa), or (XXXVIa) and (XXXVIb), is generally chosen in the range from 500:1 to 1:2, preferably from 100:1 to 1:1.

The reaction temperature is usually chosen within the range from -20 to 250°C, preferably from 0 to 200°C; in general it has been found advantageous to choose as the reaction temperature a temperature at which the reaction mixture boils; it lies within the range of the boiling temperature of the solvent used.

The pressure chosen is preferably atmospheric pressure.

The reaction time is usually chosen as a function of the reactivity of the starting materials, and of the chosen temperature; it lies generally within the range from 10 minutes to 48 hours.

If desired, the reaction can be carried out in the presence of a catalyst.

In general, the molar ratio of the catalyst to the compound of the formulae (XXXVIIb) is chosen in the range from 0.001:1 to 5:1, preferably in the range from 0.001:1 to 1:1.

Both acidic and basic catalysts are suitable.

Catalysts and solvents are as defined above.

Furthermore, the reaction is carried out, with particular preference, under an inert gas atmosphere. The inert gas used can comprise noble gases, preferably helium and argon, and also nitrogen.

It has been found advantageous in the process of the invention to use additions of binding agents such as anhydrides, especially acetic anhydride, or to use physical methods, such as distillation, for example, to remove leaving groups that are formed.

The molar ratio of anhydride to the compound of the formula (XXXVIIb) lies within the range from 0.1:1 to 5:1, preferably within the range from 0.5:1 to 2:1.

Working up and isolation are carried out as described above.

The starting compounds (XXXa) and (XXXb) are available commercially or are readily obtainable from phenols by reaction with glyoxal, for example, in accordance with the process of H.-D. Becker, K. Gustafsson, J. Org. Chem. 42, 2966 (1977).

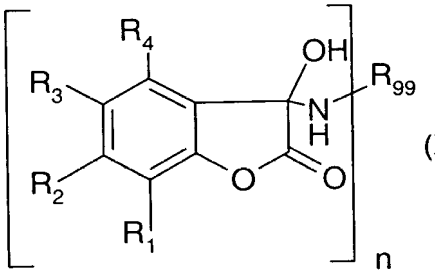
The starting compounds of the formulae (XXXI a or b) can be prepared, for example, in analogy to processes from EP-B 632 102 or Advanced Organic Chemistry, Jerry March, Ed. 1977, p. 824; those of the formulae (XXXII a or b), for example, in analogy to processes from Advanced Organic Chemistry, Jerry March, Ed. 1977, p. 817, or Advanced Organic Chemistry, Jerry March, Ed. 1977, p. 824; those of the formulae (XXXIII a or b), for example, in analogy to processes from US 2 701 252; those of the formulae (XXXIV a or b), for example, in analogy to processes from Advanced Organic Chemistry, Jerry March, Ed. 1977, p. 810; or those of the formulae (XXXV a or b), for example, in analogy to processes from

EP-B 632 102; or those of the formulae (XXXVII a or b), for example, in analogy to processes from DE-A1 1 952 962; or they are available commercially.

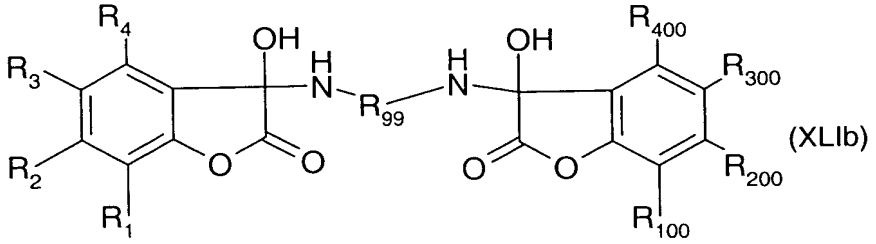
The 3-oxobenzofuran-2-ones can be prepared, for example, in analogy to known methods for the preparation of 3-unsubstituted furanones and 3-oxofuranone compounds. 3-Unsubstituted furanones, for example, can be prepared in analogy to the process of H.-D. Becker, K. Gustafsson, J. Org. Chem. 42, 2966 (1977) from phenols by reaction with glyoxal.

3-Oxobenzofuran-2-ones (XXXVIa) and (XXXVIb) can be prepared, moreover, by oxidizing 3-unsubstituted benzofuran-2-ones, or by oxidizing 3-hydroxy-3-oxobenzofuran-2-ones in accordance with conventional methods for oxidizing hydroxy compounds to keto compounds. These methods are described, for example, in Houben-Weyl, Methoden der Organischen Chemie, 4th Edition, Volume 4/1a & 4/1b. In J. Org. Chem., 56, 6110 (1991), the oxidation with nitroxides is described by Z- Ma, J.M. Bobbitt. 3-Hydroxy-3-oxobenzofuran-2-ones can be prepared in analogy to the process described in US 5 614 572. In addition, 3-oxobenzofuran-2-ones can be prepared in analogy to the process described by D.J. Zwaneburg and W.A.P. Reyen in Synthesis, 624, 1976.

One particularly preferred embodiment of the present invention comprises the novel amino-hydroxy compounds of the formula (XLIa) or (XLIb)



(XLIa) or

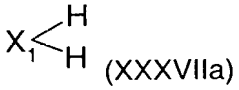


(XLIb)

in which
n is 1 or 2, and
if n is 1
R_{99} is hydrogen or substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl,
preferably A_5-A_{18}heteroaryl, C_6-C_{24}aryl unsubstituted or substituted by halogen, hydroxyl, cyano, ether, nitro, an amine, amide, imine, urethane, sulfonamide, ester, carboxylic acid, sulfonic acid radical or carboxylic salt, sulfonic salt,
especially compound of the formula (XVIII);

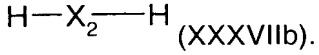
if n is 2
R_{99} is a direct bond or substituted or unsubstituted C_6-C_{24}arylene, A_5-A_{18}heteroarylene, C_5-C_{12}cycloalkyl or bi(C_6-C_{24})arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene, in which C_6-C_{24}arylene, bi(A_5-A_{18})heteroarylene, C_2-C_{24}alkenylene can be interrupted by a direct bond or by one or more intermediate units such as -CH=CH-, -CH=N-, -N=N-, -$CR_{44}R_{42}$-, -CO-, -COO-, -OCO-, -NR_{42}CO-, -$CONR_{42}$-, -O-, -S-, -SO-, -SO_2- or -NR_{42}-, and
is preferably substituted or unsubstituted C_6-C_{24}arylene or C_6-C_{24}arylene,
in which
R_{42} and R_{44} independently of one another are hydrogen, substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24} alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl.

The present invention further provides a process for preparing amine hydroxy compounds of the formulae (XLIa) or (XLIb) by reacting 3-oxobenzofuran-2-one (XXXVIa) with a compound of the formula (XXXVIIa)


(XXXVIIa)

or

3-oxobenzofuran-2-one (XXXVIa), or (XXXVIa) and (XXXVIb), with a compound of the formula (XXXVIIb)

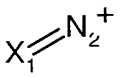

(XXXVIIb).

A further particularly preferred embodiment of the present invention comprises a process for

preparing the compound of the formulae (XLIa) or (XLIb) by reacting 3-oxobenzofuran-2-one (XXXVIa) with a compound of the formula (XXXVIIa), or 3-oxobenzofuran-2-one (XXXVIa), or (XXXVIa) and (XXXVIb), with a compound of the formula (XXXVIIb) in the presence of a catalyst, in particular of a silicate as catalyst.

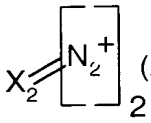
Very particular preference is further given to a process for preparing the compound of the formula (XLI) by reacting 3-oxobenzofuran-2-one (XXXVIa) with a compound of the formula (XXXVIIa), or 3-oxobenzofuran-2-one (XXXVIa), or (XXXVIa) and (XXXVIb), with a compound of the formula (XXXVIIb) in the presence of a catalyst, in particular of a silicate as catalyst, at temperatures in the range from 0 to 200°C, preferably from 20 to 160°C, with particular preference from 20 to 40°C.

The present invention further provides a process for preparing the benzofuran-2-ones (Ia), (Ib) or (Ic) in which X_1 is a compound of the formula (IV) and X_2 is a compound of the formula (X) by coupling diazotized amines to coupling components in an aqueous medium, by reacting benzofuran-2-one (XXXa) or (XXXb) with a diazonium salt of the formula (XXXVIIIa)



(XXXVIIIa)

or benzofuran-2-one (XXXa), or (XXXa) and (XXXb), with a diazonium salt of the formula (XXXVIIIb)



(XXXVIIIb).

The reaction is normally started by bringing the diazonium salt, generally in the form of a solution, into contact with benzofuran-2-one, for example by mixing the starting materials or by adding one starting material dropwise to the other. The sequence of the addition is generally unimportant; preferably, benzofuran-2-one is added to a solution of the diazonium salt. Benzofuran-2-one can be in the form of a solution, dispersion or suspension, preferably a solution.

For the preparation of the benzofuran-2-ones of the formula (Ia) it is common to choose the molar ratio of a compound (XXXa) to a compound of the formula (XXXVIIIa) in the range from 0.8:1 to 3:1; preferably, the molar ratio lies within the range from 0.9:1 to 2:1.

For the preparation of the benzofuran-2-ones of the formulae (Ib) or (Ic), the molar ratio of a compound (XXXa) or (XXXa) and (XXXb) to a compound of the formula (XXXVIIIb) is generally chosen in the range from 1:0.9 to 1:0.2; preferably, the molar ratio is situated within the range from 1:0.66 to 1:0.4

The solvent chosen for the solution, dispersion or suspension is generally water, sodium acetate, sodium formate or an organic solvent such as formic, acetic, propionic acid, especially glycol ethers such as ethylene glycol monoethyl ether, or mixtures of these solvents, especially mixtures containing water.

The molar ratio of solvent to the compound (XXXa), or (XXXa) and (XXXb), is generally chosen in the range from 500:1 to 1:2, preferably from 100:1 to 1:1.

The reaction temperature is usually chosen in the range from -20 to 100°C, preferably from 0 to 50°C.

The pressure chosen is preferably atmospheric pressure.

The reaction time is usually chosen as a function of the reactivity of the starting materials, and of the chosen temperature, and is generally situated within the range from 10 minutes to 48 hours.

If desired, the reaction can be carried out in the presence of nonionogenic, anionic or cationic surface-active substances, which may have a cloud point in aqueous medium. If desired, it is also possible to use further auxiliaries, such as natural or synthetic resins or resin derivatives, or additives customary for paints, printing inks or plastics.

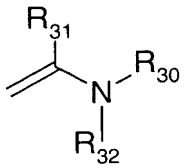
The product can be isolated in accordance with the customary methods, such as by adding water and then carrying out filtration, for example, or directly by filtration. If desired, the filter residue can be washed with, for example, water and/or an organic solvent such as methanol, and then dried.

If desired, in one preferred embodiment of the process of the invention, the crude product can be heated at boiling, or recrystallized, in an organic solvent and then isolated. In general, for this purpose, the crude product is admixed with an organic solvent and the resulting mixture is heated at boiling for from 1 to 24 hours. It is subsequently cooled, usually to a

temperature in the range from -20 to 40°C, and the mixture is filtered, the product being obtained as the filter residue. Normally, the filter residue is subsequently dried in vacuo in the range from 40 to 200°C, preferably in the range from 60 to 120°C.

The starting materials of the formulae (XXXVIIIa) or (XXXVIIIb) are readily obtainable in accordance, for example, with Houben-Weyl, Volume 10/3.

The present invention likewise provides a process for preparing benzofuran-2-ones (Ia), (Ib) or (Ic) in which X_1 is X_{10} and X_1 is a compound of the formula (V)



(V)

in which

R_{31} is hydrogen or $-NR_{89}R_{90}$, in which

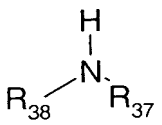
R_{30}, R_{32}, R_{89} and R_{90} independently of one another are hydrogen, C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_5-C_{24}aryloxy, -thio or A_5-A_{18}hetereoaryloxy, -thio, or are C_6-C_{24}aryl-substituted secondary or tertiary amine or C_6-C_{24}aryl, or with X_2 is a compound of the formula (XI), by formylation and subsequent reaction with an amine,
by reacting benzofuran-2-one (XXXa) with a formylating reagent of the formula (XXXVIII)

$$R_{35}C(OR_{36})_3 \qquad \text{(XXXVIII)}$$

in which

R_{35} and R_{36} independently of one another are substituted or unsubstituted C_1-C_{24}alkyl, C_5-C_{12}cycloalkyl, C_2-C_{24}alkenyl, C_6-C_{24}aryl, C_7-C_{25}aralkyl, or A_5-A_{18}heteroaryl,

and with a compound of the formula (IXLa)

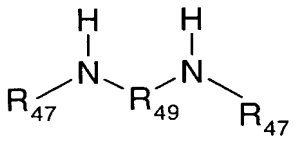


(IXLa)

or

reacting two benzofuran-2-ones (XXXa), or benzofuran-2-ones (XXXa) and (XXXb), with a formylating reagent of the formula (XXXVIII)

and with a compound of the formula (IXLb)



(IXLb)

The compounds of the formula (Ia), (Ib) or (Ic) are prepared in close analogy to a process described by O.S. Wolfbeis, H. Junek, in Z. Naturforsch. 34b, 283-289, 1979 by one-pot coupling reaction of three compounds, a methylene-active compound with a formylating reagent and an amine.

The other process parameters of the preparation correspond to those above for the preparation of the compound (Ia), (Ib) or (Ic) from benzofuran-2-one (XXXa) or (XXXa) and (XXXb) with a compound of the formula (XXXI a or b), (XXXII a or b), (XXXIII a or b), (XXXIV a or b), (XXXV a or b) or (XXXVII a or b).

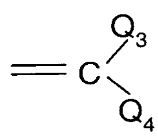
Of course, many benzofuran-2-ones of the invention can also be prepared from other benzofuran-2-ones of the invention by chemically modifying their substituents as functional groups without altering the benzofuran-2-one parent structure. The person skilled in the art knows countless methods with which substituents can be converted into other substituents, examples being those methods disclosed in the series "Compendium of Organic Synthetic Methods" (Wiley & Sons, New York, from 1971). Owing to the known reactivity of benzofuran-2-one, judicious reaction conditions are those under which it is not anticipated that its lactone bonds will be cleaved or its double bond reduced. Depending on the nature of their substituents, the compounds of the formulae (Ia), (Ib) or (Ic) can be used to prepare novel benzofuran-2-ones of the formulae (Ia), (Ib) or (Ic). For example, novel ester derivatives or amide derivatives can be prepared in accordance with conventional synthesis methods for preparing esters or amides, as is described, for example, in Organic Syntheses, Collective Vol. I-VII. Preference is given in particular to esters prepared by transesterifying or esterifying compounds of the formula/formulae (Ia), (Ib) or (Ic) using, for example, various alcohols under conventional synthesis conditions and catalysis conditions, such as, for

example, at temperatures from 0°C to 200°C, with alcohol amounts of from 1 to 200 equivalents per equivalent of the compound of the formulae (Ia), (Ib) or (Ic), in the absence or presence of a solvent.

The present invention further provides a composition of matter comprising a high molecular weight organic material and at least one compound of the formulae (Ia), (Ib) or (Ic)
in which

X_1 is X_{10}, where X_{10} is a substituted or unsubstituted hydrazone or imine radical, or

is a methylene radical

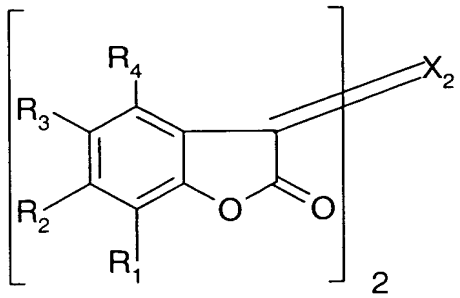


in which

Q_3 and Q_4 are Q_6 and Q_7 and independently of one another are hydrogen or substituted or unsubstituted C_1-C_{24}alkyl, -CO-(C_1-C_{24}alkyl), -CO-O-(C_1-C_{24}alkyl), C_1-C_{24}alkoxy, C_1-C_{24}alkylthio, C_5-C_{12}cycloalkyl, C_5-C_{12}cycloalkoxy, C_5-C_{12}cycloalkylthio, C_2-C_{24}alkenyl, a primary or secondary amine radical, C_6-C_{24}aryl, -CO-O-(C_6-C_{24}aryl), -CO-(C_6-C_{24}aryl), C_6-C_{24}aryloxy, C_6-C_{12}arylthio, C_7-C_{25}aralkyl or A_5-A_{18}heteroaryl,
or
Q_3 and Q_4 together are a lactam, quinomethylene, hydantoin, acenaphthenequinone, azlactone, pyrazolonyl, barbituric acid, isoindolinone or isoindoline radical, or a composition as defined below, in a colouringly effective amount.

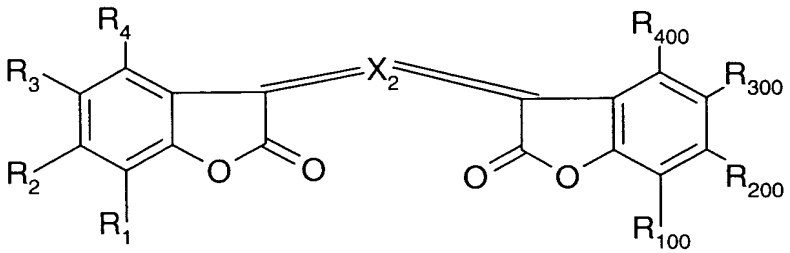
Dimeric benzofuran-2-ones are known in part from WO 92/08703, as is their use as antioxidants.

The present invention further provides compositions consisting of from 2 to 10, preferably 2 or 3, compounds of the formulae (Ia), (Ib) and/or (Ic) and/or (XLIa) and/or (XLIb) and/or dimeric benzofuran-2-ones of the formulae (XLIIa) and/or (XLIIb)



(XLIIa)

or



(XLIIb)

in which

X_2 is (C_6-C_{24})arylene, (A_5-A_{18})heteroarylene or a divalent polymethylidene, polyether, polyimine, polyamine radical, or bi(C_6-C_{24})arylene or bi(A_5-A_{18})heteroarylene, the bi(C_6-C_{24})arylene or bi(A_5-A_{18})heteroarylene radical being attached directly or via a substituted or unsubstituted carbon, nitrogen, oxygen or (-N=N-)-diradical.

The molar ratio of the composition consisting of two compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) and/or (XLIb) is usually within the range from 99:1 to 1:99.

The compositions containing 2 to 10 compounds can be prepared from the individual compounds by methods of mixing known per se.

One preferred embodiment of the present invention comprises a process for preparing compositions by reacting from 2 to 10, with particular preference 2 to 3, different benzofuran-2-ones (XXXa) with a compound of the formulae (XXXIa), (XXXIIa), (XXXIIIa), (XXXIVa) or (XXXVa),

or

by reacting from 2 to 10, with particular preference 2 to 3, different 3-oxobenzofuran-2-ones

(XXXVIa) with a compound of the formula (XXXVIIa).

The compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) are judiciously used in an amount of from 0.01 to 70% by weight, usually from 0.01 to 30% by weight, preferably from 0.01 to 10% by weight, based on the high molecular weight organic material to be coloured.

In a further embodiment of the process of the invention it is also possible if desired to admix two or more compounds, preferably from 2 to 10 and, with particular preference, 2 or 3 compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) to the high molecular weight organic or inorganic material.

The invention therefore further provides a composition of matter comprising a high molecular weight organic material and at least one compound of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) or a composition consisting of compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) in an amount effective for colouring, generally in the range from 0.01 to 70% by weight, in particular from 0.01 to 30% by weight, preferably from 0.01 to 10% by weight, based on the high molecular weight organic material.

Further, the present invention provides for the individual use of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) as colorants, especially for colouring or pigmenting high or low molecular weight organic or inorganic material, especially the use of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) and of the compositions of the invention, and also the compositions of matter, for preparing inks or colorants for coating materials, printing inks, mineral oils, lubricating greases or waxes, or dyed or pigmented plastics, non-impact-printing material, colour filters, cosmetics, toners.

It is, however, likewise possible to use the compositions of the invention comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIIb), (XLIa) or (XLIb). Compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) can also be combined with colorants from a different chemical class, for example with dyes or pigments as selected, for example, from the group consisting of the diketopyrrolopyrroles, quinacridones, perylenes, dioxazines, perinones, coumarins, anthraquinones, indanthrones, flavanthrones, indigos, thioindigos, quinophthalones, isoindolinones, isoindolines, phthalocyanines, metal complexes, azo pigments and azo dyes.

Depending on the nature of their substituents and of the polymer to be coloured, compounds

of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) can be used as polymer-soluble dyes or as pigments. In the latter case it is advantageous to convert the as-synthesized products into a finely disperse form. This can be accomplished in a conventional manner. Depending on the compound and intended use, it is found advantageous to use the colorants as toners or in the form of preparations.

The high molecular weight material can be organic or inorganic and can comprise synthetic substances and/or natural substances. They can be, for example, natural resins or dry oils, rubber or caseine, or modified natural substances such as chloro rubber, oil-modified alkyd resins, viscose, or cellulose ethers or cellulose esters such as ethyl cellulose, cellulose acetate, cellulose propionate or cellulose butyrate, cellulose acetobutyrate and also nitrocellulose, but especially wholly synthetic organic polymers (thermosets and thermoplastics) as are obtainable by addition polymerization, for example by polycondensation or polyaddition. The class of the polymers includes, for example, polyolefins such as polyethylene, polypropylene, polyisobutylene, and also substituted polyolefins such as addition polymers of monomers such as vinyl chloride, vinyl acetate, styrene, acrylonitrile, acrylates, methacryaltes, fluoropolymers such as polyfluoroethylene, polytrifluorochloroethylene or tetrafluoroethylene-hexafluoropropylene copolymer, and also addition copolymers of the abovementioned monomers, especially ABS (acrylonitrile/butadiene/styrene) or EVA (ethylene/vinyl acetate). From the series of the polyaddition resins and polycondensation resins it is possible, for example, to use condensates of formaldehyde with phenols, known as phenolic resins, and condensates of formaldehyde and urea or thiourea, and also melamine, known as amino resins, and also the polyesters used as surface-coating resins, either saturated polyesters such as alkyd resins or unsaturated polyesters such as maleic resins, and also linear polyesters, polyamides, polyurethanes, polycarbonates, polyphenylene oxides or silicones, silicone resins.

The abovementioned high molecular weight compounds can be present individually or in mixtures as plastic compounds, as melts, or in the form of spinning solutions. They can also be present in the form of their monomers or in the polymerized state in dissolved form as film-formers or binders for coating materials or printing inks, such as, for example, linseed oil varnish, nitrocellulose, alkyd resins, melamine resins and urea-formaldehyde resins or acrylic resins.

The present invention therefore further provides for the use of the compositions of the invention comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) for preparing

inks, for printing inks in printing processes, for flexographic printing, screen printing, packaging printing, security ink printing, gravure printing or offset printing, for pre-press stages and for textile printing, for office applications, domestic applications or graphics applications, such as for paper goods, for ballpoint pens, felt tips, fibre tips, card, wood, (wood)stains, metal, inking pads or inks for impact printing processes (with impact-pressure ink ribbon), for the preparation of

colorants for coating materials, for industrial or commercial use, for textile decoration and industrial marking, for roller coatings or powder coatings or for automotive finishes, for high-solids (low-solvent), waterborne or metallic coating materials or for pigmented formulations for aqueous paints, for mineral oils, lubricating greases or waxes, for the preparation of

coloured plastics for coatings, fibres, platters or mould carriers, for the preparation of

non-impact-printing material for digital printing processes, for the thermal wax transfer printing process, the ink-jet printing process or for the thermal transfer printing process, and also for the preparation of

polymeric ink particles, toners, dry copy toners, liquid copy toners or electrophotographic toners.

The present invention additionally provides inks comprising high molecular weight organic material and a colouringly effective amount of the compound of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) or of the composition consisting of compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

Processes for preparing inks in particular for ink-jet printing are common knowledge.

The inks can be prepared, for example, by mixing the compounds of the invention with polymeric dispersants.

The mixing of the compounds of the invention with the polymeric dispersant takes place preferably in accordance with conventional methods of mixing, such as stirring or mechanical mixing; preferably it is advisable to use intensive mixers such as an Ultra-Turrax.

When mixing the compounds of the invention with polymeric dispersants it is judicious to use a water-dilutable organic solvent.

The weight ratio of the compounds of the invention to the ink is judiciously chosen in the range from 0.0001 to 75% by weight, preferably from 0.001 to 50% by weight, based on the overall weight of the ink.

The present invention therefore also provides a process for preparing inks by mixing with one another high molecular weight organic material and a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) or the compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

Further, the present invention provides colorants comprising high molecular weight organic material and compounds of the formula (I) and/or (XLI) and/or compounds of the formula (XLII) of the invention, or a composition of the invention, in a colouringly effective amount.

The present invention provides, moreover, a process for preparing colorant by mixing a high molecular weight organic material and a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) of the invention or compositions of the invention comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

In addition, the present invention provides coloured plastics or polymeric ink particles comprising high molecular weight organic material and compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), in a colouringly effective amount.

Furthermore, the present invention provides a process for preparing coloured plastics or polymeric ink particles by mixing with one another a high molecular weight organic material and a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

The colouring of the high molecular weight organic substances with the colorants of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or with the compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), takes place, for example, by mixing such a colorant in the form, if desired, of masterbatches into these substrates using roll mills, mixing or grinding apparatus to dissolve

or finely disperse the colorant in the high molecular weight material. The high molecular weight material with the admixed colorant is subsequently processed by organic methods known per se, such as, for example, by calendering, compression, extrusion, coating, spinning, casting or injection moulding, whereby the coloured material acquires its ultimate shape. The admixing of the colorant can also be carried out directly prior to the actual processing step, for example by continuously metering in a pulverulent colorant of the invention and a granulated, high molecular weight organic material, and also, if desired, additional substances such as additives, simultaneously and directly into the inlet zone of an extruder where the mixing-in takes place just prior to processing. In general, however, prior mixing of the colorant into the high molecular weight organic material is preferable, since more uniform results can be obtained.

It is frequently desired to incorporate plasticizers into the high molecular weight compounds, prior to shaping in order to produce non-rigid mouldings or to reduce their brittleness. Examples of useful plasticizers are esters of phosphoric acid, phthalic acid or sebacic acid. In the process of the invention, the plasticizers can be incorporated into the polymers before or after the colorant has been incorporated. It is further possible, for the purpose of achieving different hues, to add to the high molecular weight organic materials not only the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or the compositions of the invention, constituents such as white, colour or black pigments in any desired amounts.

To colour coating materials and printing inks, the high molecular weight organic materials and the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions of the invention, together if desired with additives such as fillers, dyes, pigments, siccatives or plasticizers, are finely dispersed or dissolved in a common organic solvent or solvent mixture. This can be accomplished by dispersing or dissolving the individual components by themselves or else more than one together and only then to combine all the components. Processing is effected by customary methods, for example by spraying, film-drawing or one of the many printing methods, after which the coating material or printing ink, after drying beforehand if desired, is subjected judiciously to thermal or radiative curing.

Where the high molecular weight material to be coloured is a coating material, it can be a standard paint or else a speciality paint, for example an automotive paint, preferably a metallic effect coating containing, for example, metal particles or mica particles.

Preference is given to the coloration of thermoplastics, including in particular those in the

form of fibres, and of printing inks. Preferred high molecular weight organic materials which can be coloured in accordance with the invention are, very generally, polymers having a dielectric constant ≥ 2.5, especially polyesters, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) or acrylonitrile/butadiene/styrene (ABS). Particular preference is given to polyesters, polycarbonate, polystyrene, ABS and PMMA. Very particular preference is given to polyesters, ABS, polycarbonate or PMMA, especially aromatic polyesters obtainable by polycondensation of terephthalic acid, such as polyethylene terephthalate (PET) or polybutylene terephthalate (PBTP), for example.

Particular preference, furthermore, is given to the colouring of low molecular weight organic material such as mineral oils, lubricating greases and waxes using the compounds of the invention.

Moreover, the present invention provides non-impact-printing material comprising high molecular weight organic material and a compound of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), in a colouringly effective amount.

Furthermore, the present invention provides a process for preparing non-impact-printing material by mixing with one another a high molecular weight organic material and a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

Furthermore, the present invention provides toners comprising high molecular weight organic material and a compound of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), in a colouringly effective amount.

Moreover, the present invention provides a process for preparing toners by mixing with one another a high molecular weight organic material and a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb).

In one particular embodiment of the process of the invention, toners, coating materials, inks

or coloured plastics are prepared by processing masterbatches of toners, coating materials, inks or coloured plastics in roll mills, mixing or grinding apparatus.

In the present invention, a colouringly effective amount of the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) or compositions comprising compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb) is generally from 0.0001 to 99.99% by weight, preferably from 0.001 to 50% by weight and, with particular preference, from 0.01 to 50% by weight, based on the overall weight of the material coloured or pigmented with them.

When the compounds of the formulae (Ia), (Ib), (Ic), (XLIIa), (XLIIb), (XLIa) or (XLIb), or the compositions of the invention, are present dissolved in the polymers employed, they are notable for a clean hue, high colour strength, good light, heat and weather fastness, especially in PET, PMMA, PS and PC, and, if appropriate, for in some cases high fluorescence. The colorations obtained, for example, in thermoplastics or thermosets, fibres, coating materials or printing inks are notable for a clean hue, high colour strength, high saturation, high transparency, good fastness to overcoating, migration, rubbing, light, weathering and especially heat, and good gloss. The colorants possess good dispersibility and generally good solubilities in organic solvents. In mixtures containing the compounds of the invention, beautiful colour shades are obtained.

The compositions of the invention may exhibit advantages in terms of applications properties over individual compounds.

The examples which follow illustrate the invention without in any way restricting it:

The preparations of 5,7-di-tert-butyl-3H.-benzofuran-2-one, 5-methoxy-7-tert-butyl-3H-benzofuran-2-one and methyl 3-tert-butyl-3H-benzofuran-2-on-5-yl)propionate take place in analogy to H.-D. Becker, K. Gustafsson: J. Org. Chem. 42, 2966 (1977).

Example 1a: A 15 l multi-necked vessel with stirrer, dropping funnel, water separator, condenser and thermometer is charged with stirring and in succession with 300 ml of toluene, 212 g of 97% 2,4-di-tert-butylphenol (Aldrich 99%), 121.9 ml of 50% strength aqueous glyoxylic acid and 0.5 g of p-toluenesulfonic acid monohydrate. The reaction mixture is subsequently refluxed vigorously with thorough stirring. This is accompanied by the separation of the water present in the glyoxylic acid, and the water of reaction from the

first stage. After a reflux time of about 3 h, the separation of water ends, to leave a homogeneous, pale yellow solution of 5,7-di-t-butyl-3-hydroxybenzofuran-2-one. Thereafter, the toluene is distilled off under atmospheric pressure and with a heating-bath temperature of up to 142°C. The crystalline solid is subsequently dried at 80°C/50 mbar.

Example 1b: 5,7-Di-tert-butyl-3-hydroxybenzofuran-2-one, 30 g (114 mmol), prepared in accordance with Example 1a, is dissolved in 200 ml of dimethyl sulfoxide. 54 ml (574 mmol) of acetic anhydride is added to the solution over 2 minutes with vigorous stirring, and stirring is continued for 15 hours at from 25 to 27°C. With stirring, the reaction mixture is poured into 2 litres of water and stirred for 2 hours. The precipitate is filtered off with suction and washed with 1 litre of water, then sodium chloride solution (25% by weight) and then with 1 litre of water. The precipitate is subsequently dried at 80°C/15 mbar. This gives 31.10 g of orange crystals of 5,7-di-tert-butyl-3-oxobenzofuran-2-one.

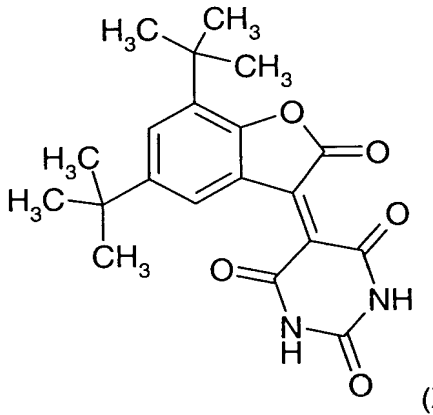
Example 1c: Synthesis of 3-oxo-furan-2-one derivatives via oxallyl chloride, general instruction

0.5 mol of the hydroxyaromatic compound is dissolved in 200 ml of dichloromethane and that solution is then added over 2 hours to a solution of 0.55 mol of oxallyl chloride in 200 ml of dichloromethane. The solution is heated to 35°C, then 3 portions each of 0.5 g of aluminium chloride (Fluka) are added and the mixture is stirred for 17 hours. After cooling, the mixture is filtered with suction to isolate the residue, which is washed with 3 times 50 ml of hexane. A second fraction of the product can be obtained by concentrating the filtrates and then washing the residues with hexane. For purification, the product can be recrystallized from glacial acetic acid or used directly. Additional purification can be achieved by reaction with sodium hydrogen sulfide, recrystallization from water, and subsequent acidic hydrolysis of the adduct using mineral acids.

Product	Yield	Properties
5,7-Di-tert-butyl-3-oxobenzofuran-2-one	65%	yellow crystals
3-Oxo-2-naphthofuranone	76%	orange crystals

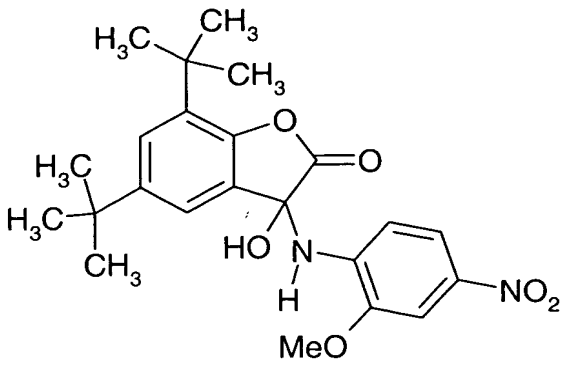
5-t-Butyl-7-methoxy-3-oxo-benzofuranone	46%	orange crystals
3-Oxo-1-naphthofuranone	73%	orange crystals
5-Hydroxy-3-oxo-β-naphthofuranone	94%	orange crystals
6-Hydroxy-3-oxobenzofuranone	17%	yellow crystals

Example 2: 5,7-Di-tert-butyl-3-oxobenzofuran-2-one, 4 g (15.4 mmol), prepared as in Example 1b, is dissolved together with barbituric acid, 2.14 g, (Fluka) in 100 ml of acetic acid and the solution is boiled under reflux for 17 hours. The solvent is subsequently distilled off with 60 mbar/60°C and then 250 ml of methanol are added to the residue. A bright yellow product is precipitated which is filtered off with suction and dried in vacuo at 50 mbar/40°C. This gives 0.17 g of a compound of the formula (XLIV)



(XLIV)

Example 3: 5,7-Di-t-butyl-3-oxobenzofuran-2-one, 4 g (15.4 mmol), prepared in accordance with Example 1b, and 2-methoxy-4-nitroaniline, 2.56 g (15.4 mmol) (Fluka) are dissolved in 100 ml of toluene. 50 mg of para-toluenesulfonic acid (Fluka) are added as catalyst to this solution, which is then boiled under reflux for 6 hours. The solvent is subsequently evaporated off under 60°C/75 mbar vacuum and the residue is recrystallized from 100 ml of methanol. This gives 2.08 g of dark yellow crystals of the formula (XLV)



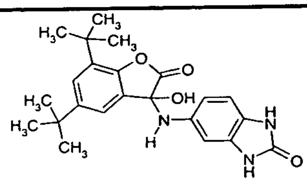
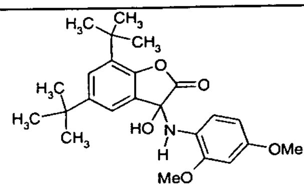
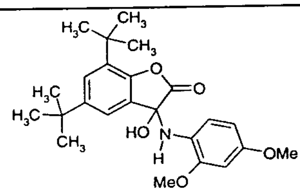
(XLV)

Example 4-6: 5,7-Di-tert-butyl-3-oxobenzofuran-2-one, 4 g (15.4 mmol), prepared in accordance with Example 1b, and 2-methoxy-4-nitroaniline, 2.56 g (15.4 mmol) (Fluka), are dissolved in 100 ml of cyclohexane. 4 g of a silicate is added as catalyst (see Table 1) to this solution, which is subsequently stirred at from 25 to 27°C for 24 h. The solvent is then evaporated off at 60°C under 100 mbar vacuum and the residue is washed with 100 ml of methanol and dried in vacuo (50 mbar) at 27°C. This gives 2.08 g of dark yellow crystals of the formula (IL). Table 1.

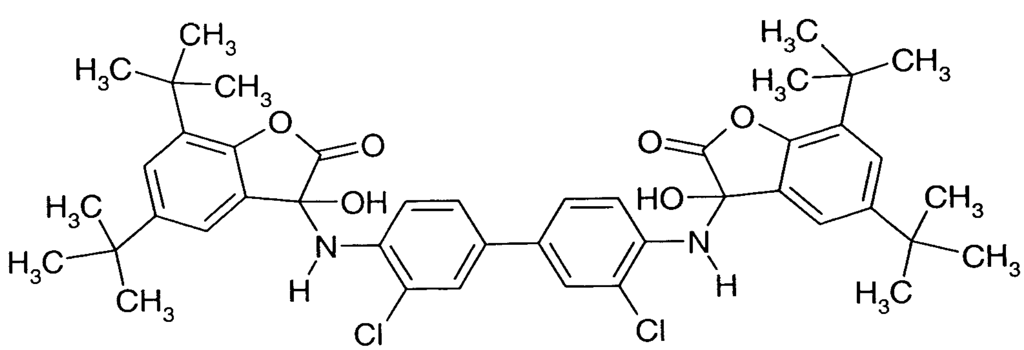
Catalyst	Yield	Example
Fulkat 40 from Pontecchio Marconi	3.89 g	4
Catalyst K10 from Süd-Chemie	3.88 g	5
Catalyst Rudex from Rudex Nebelova Bratislava	3.57 g	6

Example 7-9: Preparation as for Examples 4-6 but with the difference that silicate K10 is used as catalyst for Examples 7-9 and, instead of the 2-methoxy-4-nitroaniline, use is made in Example 7 of 5-aminobenzimidazolone (Clariant), 2.29 g (15.4 mmol),
in Example 8 of 2,4-dimethoxyaniline (Aldrich), 2.36 g (15.4 mmol), under the same conditions, and
in Example 9 of 3-nitroaniline (Aldrich), 2.21 g (15.4 mmol), using xylene as solvent at 140°C.

Table 2:

Product	Yield	Example
 (XLVI)	1.41 g bright yellow powder	7
 (XLVII)	2.82g orange crystals.	8
 (XLVIII)	1.82 g yellow crystals	9

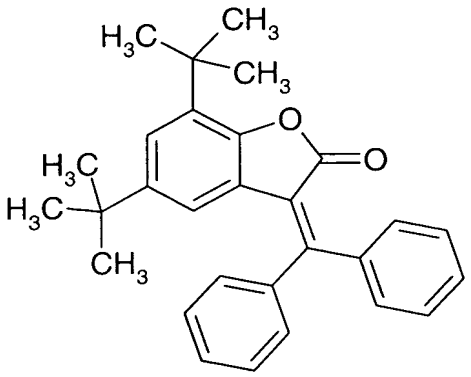
Example 10: 5,7-Di-t-butyl-3-oxobenzofuran-2-one, 4 g (15.4 mmol), prepared in accordance with Example 1b, and 2,2'-dichlorobenzidine, 1.92 g, are dissolved in 100 ml of ethanol and the solution is boiled under reflux at 76°C for 13 hours. The solvent is then evaporated off at 50°C/175 mbar and the residue is washed with 100 ml of methanol and dried under 50 mbar at 27°C. This gives 0.58 g of yellow crystals of the formula (L)



(L)

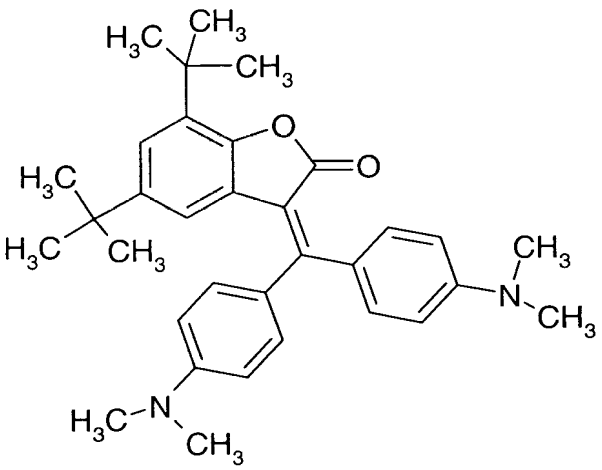
Example 11: 5,7-Di-tert-butyl-3H-benzofuran-2-one, 4.93 g, prepared as in Example 1a and dissolved in 20 ml of toluene, is added to a suspension of sodium hydride, 0.88 g (Fluka

pract.). Subsequently, benzophenone (Fluka purum), 3.46 g, is added. The resulting mixture is heated to boiling and stirred at boiling temperature for 15 hours. The mixture is then admixed with acetic acid (Fluka puriss.), 1.32 g, then cooled to room temperature and extracted with 50 ml of toluene. The organic phase is dried over Na_2SO_4, and concentrated and the residue is crystallized from methanol. The crystals are filtered off and the filter residue is dried in a drying oven at 60°C. This gives 2.5 g of a yellow powder of the formula (LI)



(LI)

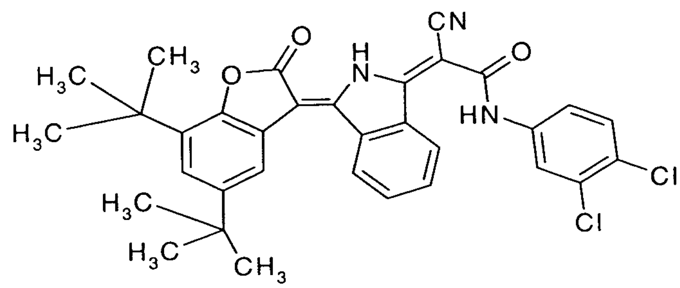
Example 12: In a manner very similar to that for the preparation of Example 11, from 4,4'-bisdimethylaminobenzophenone (Fluka purum), 1.2 g of an orange compound of the formula (LII) are obtained



(LII)

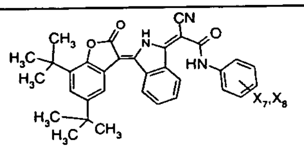
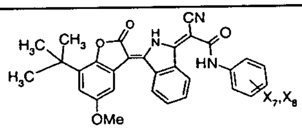
Example 13: To a boiling solution of **A,** 5,7-di-tert-butyl-3H-benzofuran-2-one, 1.5 g, prepared as in Example 1a, in 50 ml of acetic acid is added **B,** 2-cyano-N-(3,4-dichloro-phenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)acetamide, 2.43 g, prepared in accordance

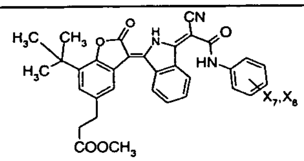
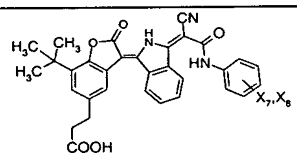
with EP 657507 A2. The mixture is stirred further under reflux for 19 hours, then cooled to room temperature and subsequently filtered. The filter residue is washed with acetic acid and then with water. The moist filter residue is dried in a vacuum drying oven at 80°C. This gives 2.74 g of an orange powder of the formula (LIII), which when incorporated into PET gives an orange colour.

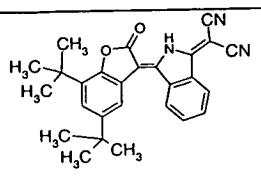
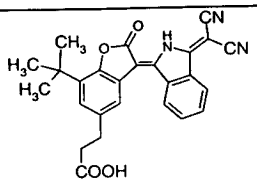


(LIII)

Example 14a-l: In analogy to the process in Example 13, the compounds of Table 3 are prepared:

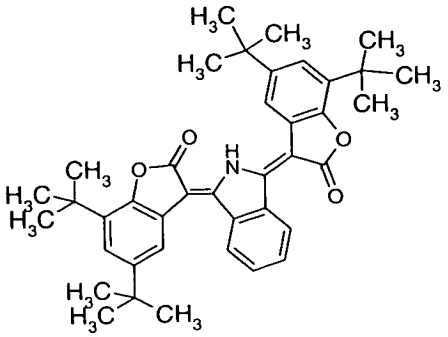
	Starting material A	Starting material B	Colour	Example
 (LIV) where X_7 = 4-Cl	A	1-[Cyano(4-chlorophenyl-carbamoyl)methylene]-3-iminoisoindoline Prepared in analogy to DE 2814526	orange	14a
see above (LIVa) where X_8 =2-COOCH3	A	2-Cyano-N-(2-carboxymethyl-phenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)-acetamide Prepared in analogy to DE 2814526	orange	14b
 (LV) where X_7 = -Cl	5-tert-Butyl-7-methoxy-3H-benzofuran-2-one Prepared in analogy to H.-D. Becker, K.Gustaffsson, J.Org.Chem. 42, 299 (1977)	2-Cyano-N-(-4-chloro-phenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)-acetamide	red	14c
see above (LVI) where X_7,X_8= 3,4-Bis-Cl	5-tert-Butyl-7-methoxy-3H-benzofuran-2-one	B	red	14d
see above (LVII) where X_7 =2-$COOCH_3$	5-tert-Butyl-7-methoxy-3H-benzofuran-2-one	2-Cyano-N-(2-carboxymethylphenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)acetamide	red	14e

	Starting material A	Starting material B	Colour	Example
 (LVIII) where X_7 = 4-Cl	5-tert-Butyl-7-methypropionic acid ester-3H-benzofuran-2-one Prepared in analogy to Synlett S1, (1999) pp. 863-864	2-Cyano-N-(4-chloro-phenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)-acetamide	orange	14f
see above (LIX) where X_7,X_8= 3,4-Bis-Cl	5-tert-Butyl-7-methypropion acid ester-3H-benzofuran-2-one	**B**	orange	14g
see above (LX) where X_7 =2-$COOCH_3$	5-tert-Butyl-7-methypropionic acid ester-3H-benzofuran-2-one	2-Cyano-N-(2-carboxymethylphenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)acetamide	orange	14h
 (LXI) where X_7 = 4-Cl	5-tert-Butyl-7-propionic acid-3H-benzofuran-2-one Prepared in analogy to Synlett S1, (1999) pp. 863-864	2-Cyano-N-(4-chloro-phenyl)-2-(3-imino-2,3-dihydro-1H-isoindol-1-yl)-acetamide	orange	14i
see above (LXII) where X_7,X_8= 3,4-Bis-Cl	5-tert-Butyl-7-propionic acid-3H-benzofuran-2-one	**B**	orange	14j
see above (LXIII) where X_7 =2-$COOCH_3$	5-tert-Butyl-7-propionic acid-3H-benzofuran-2-one	**B**	orange	14k

	Starting material A	Starting material B	Colour	Example
 (LXIIIa)	A	2-(3-Amino-2,3-dihydro-1H-isoindol-1-yl)malodinitrile Prepared in analogy to DE 2142245	red	14l
	5-tert-Butyl-7-methypropionic acid ester-3H-benzofuran-2-one	see above, Example 14m	red	14m

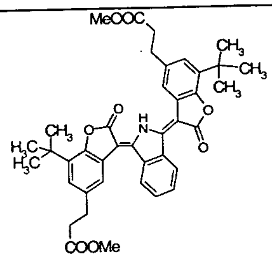
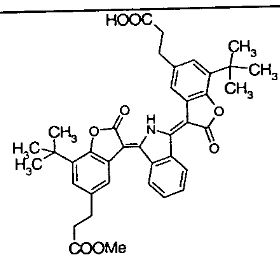
*7.4 g of the compound of the formula (LVIII), (LIX) or (LX) are heated at reflux in 300 ml of acetic acid with 3 ml of methanesulfonic acid for 56 hours. Then 100 ml of acetic acid are distilled off and the residue is poured into 1200 ml of water. The red precipitate is filtered off, washed with water and dried. This gives the compound of the formula (LXI), (LXII) or (LXIII).

Example 15: Diiminoisoindolenines, 2.1 g, (Fluka purum), and 5,7-di-t-butyl-3H-benzofuran-2-one, 6.45 g, in 60 ml of acetic acid are heated under reflux for 1.5 hours. The resulting mixture is then cooled, 50 ml of acetonitrile (Fluka puriss.) are added, and the mixture is filtered. The filter residue is washed with 50 ml of acetonitrile and 300 ml of water and dried in a drying oven at 60°C and 200 mbar. This gives 4.6 g of a violet powder of the formula (LXXX)

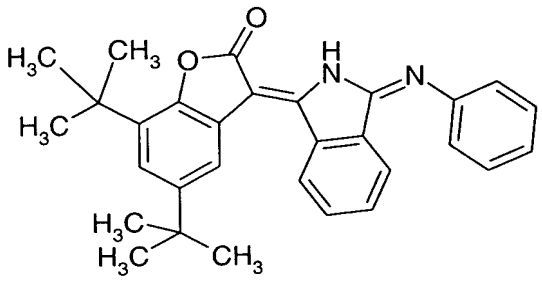


In analogy to the process in Example 15, the compounds of the Table 4 are prepared, 5,7-di-t-butyl-3H-benzofuran-2-one being replaced in Example 15a by 5-t-butyl-7-methylpropionic acid ester-3H-benzofuran-2-one and in Example 15b by 5-t-butyl-7-propionic acid-3H-benzofuran-2-one:

Table 4:

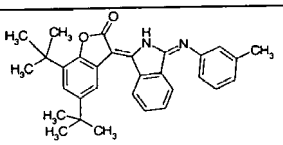
		Example	Colour
(LXXXI)		15a	violet
(LXXXII)		15b	violet

Example 16: Diiminoisoindolenine, 10 g, (Fluka purum), and 6 ml of aniline (Fluka purum) in 60 ml of ethanol are stirred under reflux for 2.5 hours. The resulting mixture is cooled to 5-10°C and filtered. The filter cake is washed with 30 ml of ethanol and subsequently dried in a drying oven at 60°C and 200 mbar, to give 7.0 g of a yellow powder. The resulting yellow powder, 1.0 g, and 5,7-di-tert-butyl-3H-benzofuran-2-one, 1.2 g, in 20 ml of ethanol are heated to 65°C and then cooled to 20-25°C. The resulting mixture is then diluted with 20 ml of methanol and filtered. The filter residue is purified by column chromatography (Merck silica gel, eluent: hexane/ethyl acetate 4:1 to 1:4) and dried in a drying oven at 60°C and 200 mbar. This gives 0.9 g of a red powder of the formula



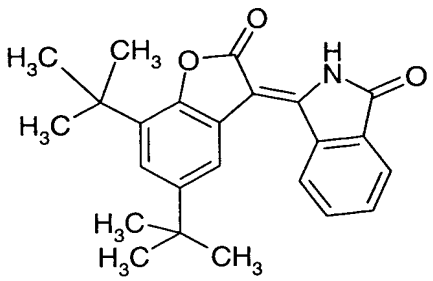
In analogy to the process in Example 16, the compound of Table 5 is prepared, aniline being replaced by 3-chloroaniline (Fluka):

Table 5:

		Example	Colour
(LXXXIIIa)		16a	yellow

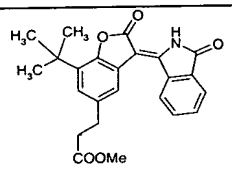
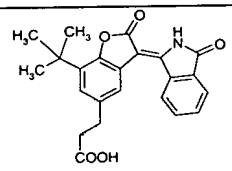
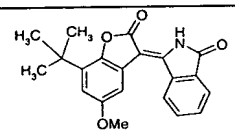
Example 17: Phthalodinitrile, 1.5 g, (Fluka purum), in 1.4 ml of a 30% sodium hydroxide solution and 30 ml of n-butanol are stirred for 2.5 hours. The pH is adjusted in the range of 6 to 7 using 37% hydrochloric acid solution, and then 5,7-di-t-butyl-3H-benzofuran-2-one, 3.1 g, is added. The mixture is stirred at 42°C for 4 hours and then cooled and filtered. The filter residue is dried in a drying oven at 60°C and 200 mbar. This gives 3.1 g of a yellow

powder of the formula (LXXXIV)



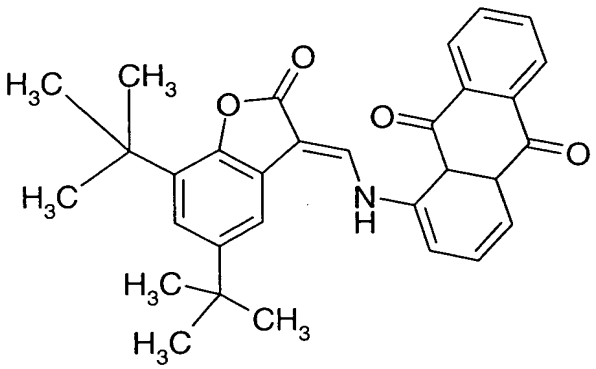
In analogy to the process in Example 17, the compounds of Table 6 are prepared, 5,7-di-t-butyl-3H-benzofuran-2-one being replaced in Example 17a by 5-t-butyl-7-methylpropionic acid ester-3H-benzofuran-2-one and in Example 17b by 5-t-butyl-7-propionic acid-3H-benzofuran-2-one and in Example 17c by 5-t-butyl-7-methoxy-3H-benzofuran-2-one:

Table 6

		Example	Colour
(LXXXIVa)		17a	yellow
(LXXXIVb)		17b	yellow
(LXXXIVc)		17c	orange

Example 18: 5,7-Di-tert-butyl-3H-benzofuran-2-one, 2.46 g, dissolved in 10 ml of acetic acid is added to 1-aminoanthraquinone (Fluka), 2.3 g, and trimethyl orthoformate (Fluka purum), 2.2 ml, dissolved in 10 ml of acetic acid. The mixture is stirred at 105°C for 2.5 hours. The

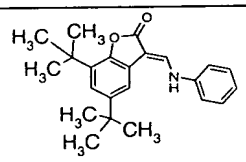
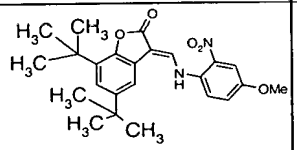
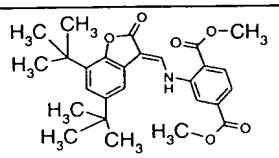
resulting mixture is subsequently cooled to room temperature and filtered. The filter residue is washed with acetic acid and then with water, and subsequently dried in a drying oven at 60°C and 200 mbar. This gives 3.7 g of a red powder of the formula (LXIV)

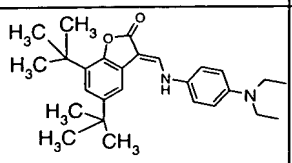
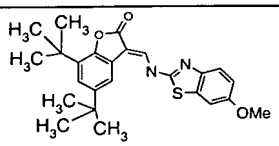
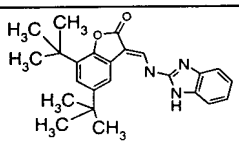
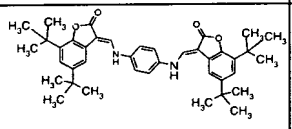
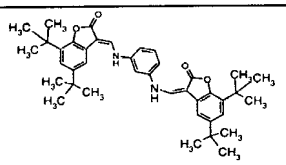
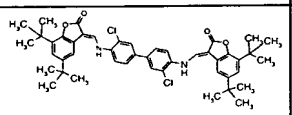


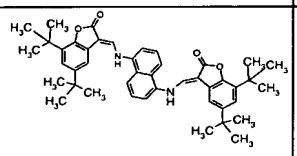
(LXIV)

Examples 19-21a-d: In analogy to the process in Example 18, the compounds of Table 7 are prepared, 1-aminoanthraquinone being replaced in each case by the corresponding compound A:

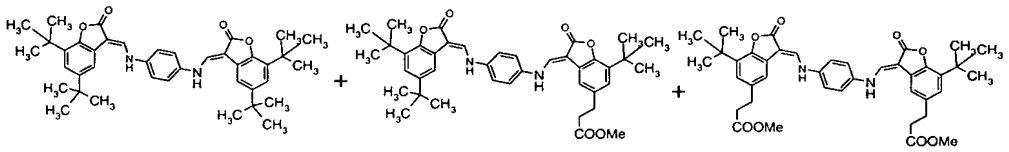
Table 7:

		A	Example	Colour
(LXV)		Aniline (FLUKA)	19	yellow
(LXVI)		2-Nitro-4-methoxyaniline (FLUKA)	20	dark red
(LXVII)		Amino-terephthalic acid (FLUKA)	21	yellow

		A	Example	Colour
(LXVIIa)		4-Amino-phthalimide AVOCADO	21a	yellow
(LXVIIb)		N,N-Diethyl-aniline FLUKA	21b	yellow
(LXVIIc)		2-Amino-methoxy-benzothiazole Aldrich	21c	yellow
(LXVIId)		2-Amino-benzimidazole Fluka	21d	yellow
(LXVIIe)		p-Phenylene-diamine (FLUKA)	21e	yellow
(LXVIIf)		m-Phenylene-diamine (FLUKA)	21f	yellow
(LXVIIg)		3,3'-Dichloro-benzidine Sigma	21g	yellow

		A	Example	Colour
(LXVIIh)		1,5-Diamino-naphthalene (FLUKA)	21h	yellow

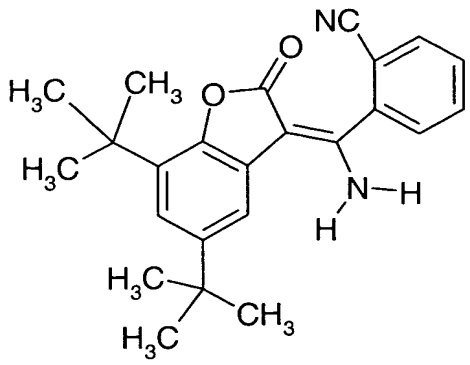
Example 21i: In analogy to the process in Example 18, the mixture of the compounds below is prepared, 5,7-di-tert-butyl-3H-benzofuran-2-one being replaced by a mixture of 5,7-di-tert-butyl-3H-benzofuran-2-one, 1.50 g, and 5-(methylpropionate)-7-tert-butyl-3H-benzofuran-2-one, 1.49 g, in a molar ratio of 1:1, and 1,4-phenylenediamine, 0.58 g (Fluka) being used instead of 1-aminoanthraquinone, the molar ratio of the mixture of 5,7-di-tert-butyl-3H-benzofuran-2-one and 5-(methylpropionate)-7-tert-butyl-3H-benzofuran-2-one to 1,4-phenylenediamine being 2:1.



Example 21j: In analogy to the process in Example 21i, the mixture of the above compounds is prepared, first 5,7-di-tert-butyl-3H-benzofuran-2-one, 1.5 g, being reacted with trimethyl orthoformate, 1.2 ml, and then a mixture of 5-(methylpropionate)-7-tert-butyl-3H-benzofuran-2-one, 1.49 g, and trimethyl orthoformate, 1.2 ml, being added. The molar ratio of 5,7-di-tert-butyl-3H-benzofuran-2-one to 5-(methylpropionate)-7-tert-butyl-3H-benzofuran-2-one is 1:1, the molar ratio of the mixture of 5,7-di-tert-butyl-3H-benzofuran-2-one and 5-(methylpropionate)-7-tert-butyl-3H-benzofuran-2-one to 1,4-phenylenediamine being 2:1.

Example 22: A mixture of potassium carbonate, 1.78 g, phthalodinitrile (FLUKA), 1.5 g, and 4.7 ml of 7N ammonia solution in 30 ml of methanol is stirred at reflux for 12 hours. Thereafter, the resulting mixture is cooled to room temperature, and 5,7-di-t-butyl-3H-benzofuran-2-one, 2.88 g, dissolved in 4.7 ml of acetic acid is added. Subsequently, the resulting mixture is stirred at reflux for 4 hours and then cooled and subsequently filtered. The filter residue is purified by column chromatography (Merck Silica gel, eluent: hexane/ethyl acetate 4:1 to 1:4) and dried in a drying oven at 60°C and 200 mbar. This gives

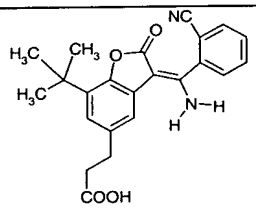
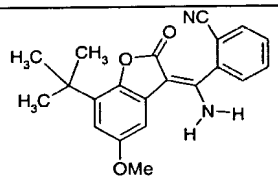
3.1 g of a red powder of the formula (LXVIII)



(LXVIII)

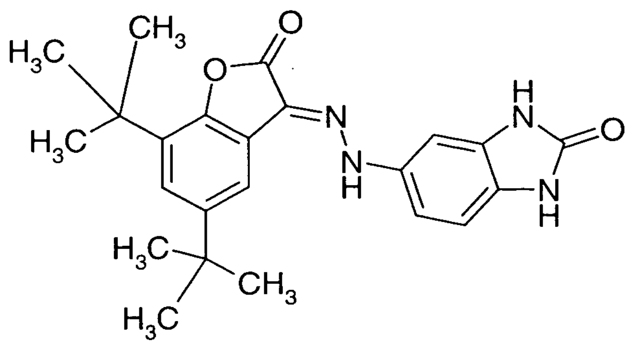
In analogy to the process in Example 22 the compounds of Table 8 are prepared, 5,7-di-t-butyl-3H-benzofuran-2-one being replaced by 5-t-butyl-7-propionic acid-3H-benzofuran-2-one in Example 22a and by 5-t-butyl-7-methoxy-3H-benzofuran-2-one in Example 22b:

Table 8:

		Example	Colour
(LXVa)		22a	orange
(LXVb)		22b	orange

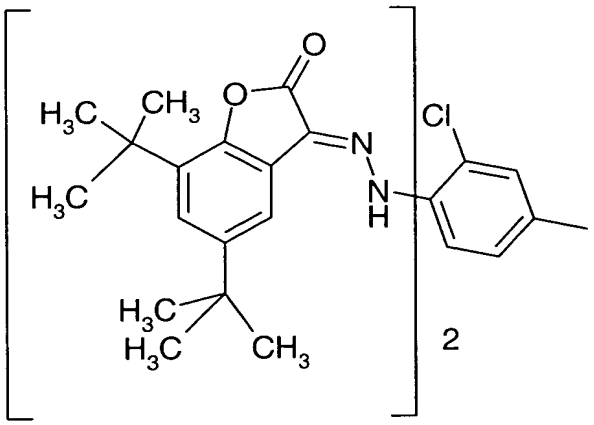
Example 23: 5-Aminobenzimidazolone (1.49 g, Aldrich) is dissolved at 40°C in 70 ml of water and 11 ml of acetic acid, and 2.7 ml of 32% hydrochloric acid are added. The solution is subsequently cooled to 5°C. Following the dropwise addition of 2.75 ml of 4N $NaNO_2$ solution and 0.5 hour of stirring at 5°C, the solution is filtered and then the excess nitrite is decomposed using sulfamic acid. Subsequently, 6 g of sodium acetate dissolved in 5 ml of

acetic acid are added. 5,7-Di-t-butyl-3H-benzofuran-2-one, 2.34 g, dissolved in 35 ml of ethylcellosolve is added dropwise at 5°C to the resulting mixture, which is then stirred at room temperature for 3 hours and subsequently at 50°C for 2 h. Thereafter, the mixture obtained is filtered at 50°C and the filter residue is washed with water and subsequently dried at 80° in a vacuum drying oven. 3.3 g of a yellow powder (LIXX) are isolated, which when incorporated in PVC gives a yellow coloration.



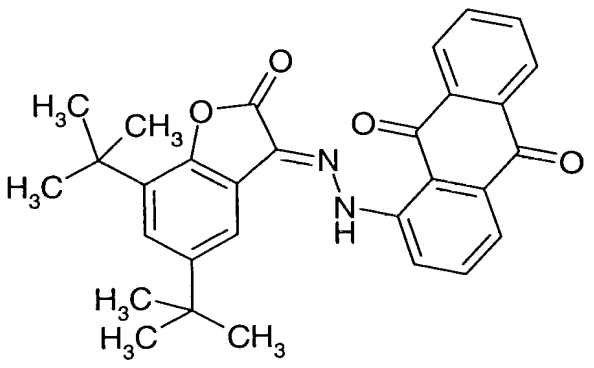
(LIXX)

Example 24: A suspension of dichlorobenzidine (Fluka purum), 2.53 g, in 27 ml of acetic acid and 3.4 ml of concentrated hydrochloric acid (32%) and 150 g of ice-water is admixed dropwise with 2.5 ml of 4N sodium nitrite solution at 0-5°C and subsequently stirred at this temperature for 45 minutes. The resulting brown suspension is admixed dropwise at 10°C over the course of 1 hour with a solution of 4.93 g of 5,7-di-t-butyl-3H-benzofuran-2-one in 70 ml of ethylcellosolve, 5 ml of acetic acid and 10 ml of saturated sodium acetate solution and is subsequently stirred at room temperature for 10 hours. The suspension obtained is filtered and the filter residue is washed with water. Subsequently, 50 ml of acetic acid are added to the filter residue, which is then heated under reflux for 2 hours. The mixture obtained is then filtered again and, subsequently, the filter residue is washed with water and dried in a vacuum drying oven at 80°C. This gives 2.15 g of a yellow-brown powder of the formula (LXX), which when incorporated into PVC gives a yellow colour.



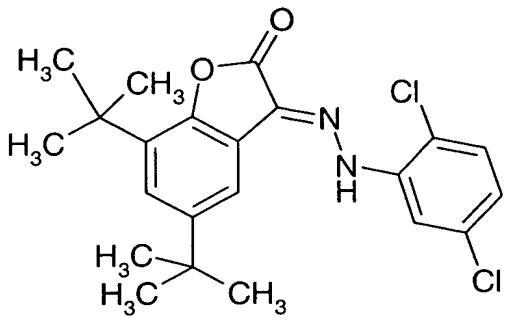
(LXX)

Example 25: A suspension of 5.75 g of aminoanthraquinone (Fluka purum) in 90 ml of acetic acid and 7.5 ml of concentrated hydrochloric acid (38%) is admixed dropwise at 0-5°C with 6.25 ml 4N sodium nitrite solution and then stirred at this temperature for 70 minutes. To the resultant mixture is added a solution of 6.16 g of 5,7-di-t-butyl-3H-benzofuran-2-one in 40 ml of 2-ethoxyethanol (Merck) at 5°C, followed by 30 g of sodium acetate, after which the mixture is stirred at room temperature for 3 h. The orange suspension obtained is diluted with 250 ml of water and filtered and the filter residue is washed with water and methanol. The filter residue is dried in a vacuum drying oven at 80°C. This gives 10.2 g of an orange powder of the formula (LXXI), which when incorporated into PET gives an orange colour.



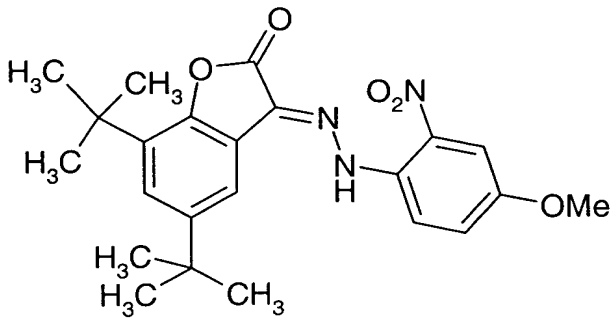
(LXXI)

Example 26: Process analogous to Example 25, but differing in that aminoanthraquinone is replaced with 2,5-dichloroaniline (Fluka purum). This gives 0.35 g of a yellow powder of the formula (LXXII), which when incorporated into PVC gives a yellow colour.



(LXXII)

Example 26a: Process analogous to Example 25, but differing in that aminoanthraquinone is replaced with 2-nitro-4-methoxyaniline (Fluka purum). This gives 5.7 g of an orange powder of the formula (LXXIII), which when incorporated into PVC gives a yellow colour.



(LXXIII),

Example 27:

3-Oxofuranone, 0.01 mol, and arylhydrazine, 0.01 mol, are dissolved in 50 ml of glacial acetic acid. With hydrazines which are very slow to react, a little sulfuric acid is added. The reaction mixture is heated under reflux until the starting compounds can no longer be detected. It is then cooled to room temperature and the precipitated product is filtered off with suction. If no product, or too little product, is precipitated, the solution is concentrated and cooled to 6°C. The product is washed with methanol and dried in vacuo.

The compounds of Examples 27a-m, 27/1 a-d, 27/2a-f, 27/3a-f, 27/4a are prepared in analogy to the above instructions of Example 27, with 3-oxofuranone being replaced respectively by 3-oxo-5,7-di-t-butylbenzofuranone and 3-oxo-1-naphthofuranone and 3-oxo-2-naphthofuranone and 5-hydroxy-3-oxo-β-naphthofuranone and 6-hydroxy-3-oxo-benzofuranone, and arylhydrazine by the respective hydrazine indicated in the examples.

In Examples 27a-m, 3-oxo-5,7-di-t-butylbenzofuranone is used instead of 3-oxofuranone:

Hydrazine (FLUKA)	m/w	λ_{max}	Colour
Example 27a : 2,4-Dinitrophenylhydrazine	440	434 nm	yellow
Example 27b : 4-Methoxy-phenylhydrazine	380	436 nm	yellow
Example 27c : Phenylhydrazine	350	420 nm	yellow
Example 27d : 4-Dimethylaminobenzoic hydrazide	421	412 nm	orange
Example 27e : Phenylsulfonic hydrazide	414	340 nm	yellow
Example 27f : 2,4,6-Trichloro-phenylhydrazine	453	394 nm	yellow
Example 27g : N-Methyl-N-phenyl-hydrazine	364	424 nm	yellow
Example 27h : 4-Chlorophenylhydrazine	384	417 nm	yellow
Example 27i : Pyridin-4-carboxylic hydrazide	379		yellow
Example 27j : Benzoic acid-2-hydrazine	394		yellow
Example 27k : 1-Naphthylhydrazine	400	445 nm	orange
Example 27l : 2-Trifluoromethyl-phenylhydrazine	418	409 nm	yellow
Example 27m: N,N-Diphenylhydrazine	426	414 nm	yellow

In Examples 27/1a-d, 3-Oxo-1-naphthofuranone is used instead of 3-oxofuranone:

Hydrazine (FLUKA)	m/w	λ_{max}	Colour
Example 27/1a : 2,4-Dinitrophenylhydrazine	378	459 nm	orange
Example 27/1b : 2-Hydrazinobenzoic acid	332	428 nm	yellow
Example 27/1c : 2,4,6-Trichloro-phenylhydrazine	391	420 nm	orange
Example 27/1d : 2-Trifluoromethyl-phenylhydrazine	356	426 nm	yellow

In Examples 27/2a-f, 3-oxo-2-naphthofuranone is used instead of 3-oxofuranone:

Hydrazine (FLUKA)	m/w	λ_{max}	Colour
Example 27/2a : 2,4-Dinitrophenylhydrazine	378	468 nm	red
Example 27/2b : 2-Hydrazinobenzoic acid	332	445 nm	orange
Example 27/2c : 2,4,6-Trichloro-phenylhydrazine	391	424 nm	yellow
Example 27/2d : 2-Trifluoromethyl-phenylhydrazine	356	432 nm	yellow
Example 27/2e : 4-Pyridinecarboxylic hydrazide	317	411 nm	yellow
Example 27/2f : 1-Naphthylhydrazine	338	469 nm	orange

In Examples 27/3a-f, 5-hydroxy-3-oxo-β-naphthofuranone is used instead of 3-oxofuranone:

Hydrazine (FLUKA)	m/w	λ_{max}	Colour
Example 27/3a : 2-Hydrazinobenzoic acid	348		yellow
Example 27/3b : 2,4,6-Trichloro-phenylhydrazine	407	429 nm	yellow
Example 27/3c: 1-Naphthylhydrazine	374	452 nm	orange
Example 27/3d: 4-Methoxyphenylhydrazine	354	440 nm	orange
Examples 27/3f: 4-Pyridinecarboxylic hydrazide	353	351 nm; 420 nm	yellow

In Example 27/4a, 6-hydroxy-3-oxo-benzofuranone is used instead of 3-oxofuranone:

Hydrazine	m/w	λ_{max}	Colour
Example 27/4 a:2-Hydrazinobenzoic acid	298		yellow

Example 28: General synthesis instructions for preparing azines, the 3-oxofuranone being replaced in Examples 28/1-3 in each case in accordance with the table below:

Hydrazine hydrate, 0.02 mol, is dissolved with 3-oxofuranone, 0.01 mol, in 20 ml of acetic acid and the solution is boiled under reflux for 5 h. If reaction is slow, 0.2 ml of conc. HCl can be added. At the end of reaction, the solution is either filtered cold or the solvent is evaporated off. The residue is washed with hexane until starting material can no longer be detected.

3-Oxofuranone	Azine		
	m/w	λ_{max}	Colour
Example 28/1 3-Oxo-5,7-di-t-butyl-benzofuranone	516	379 nm	orange
Example 28/2 3-Oxo-5-butyl-7-methoxybenzofuranone	464	463 nm	red
Example 28/3 3-Oxo-α-naphthofuranone	392	426 nm	red

General synthesis instructions A for preparing the compounds of Examples 28/4-7, the 3-oxofuranone being replaced in each case in accordance with the table below:

N,N-Diacetylpiperazine-2,5-dione, 0.01 mol, is dissolved with 3-oxofuranone, 0.01 mol, in 50 ml of dimethylacetamide, triethylamine, 0.5 ml, is added, and the mixture is stirred at 40°C. The reaction mixture is cooled and added to 150 ml of 0.5M hydrochloric acid, and the precipitate is filtered off with suction, washed with water and methanol, and then dried in vacuo.

General synthesis instructions B for preparing the compounds of Examples 28/8-9, 3-oxofuranone being replaced in each case in accordance with the table below:

Piperazine-2,5-dione, 0.01 mol, is dissolved together with 3-oxofuranone, 0.01 mol, in 50 ml of acetic anhydride, 0.5 g of sodium acetate is added, and the mixture is boiled under reflux. The precipitate is filtered off with suction at room temperature and washed with methanol and the product is dried in vacuo.

With both syntheses, the product is obtained in very good yields.

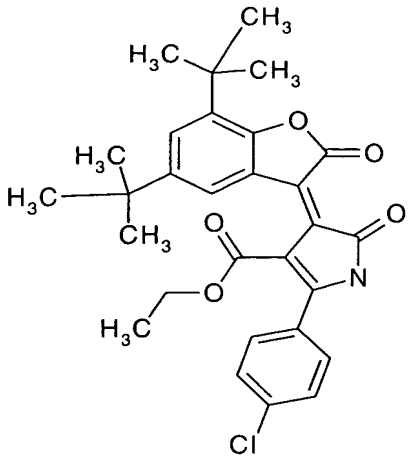
3-Oxofuranone	Synthesis method	m/w	λ_{max}	Colour
Example 28/4: 5,7-Di-t-butyl-3-oxobenzofuranone	A	598	498 nm	red
Example 28/5: 5,7-Di-t-butyl-3-oxobenzofuranone	B			
Example 28/6: β-Naphtho-3-oxofuranone	A	474	537 nm	violet
Example 28/7: 5-t-Butyl-7-methoxy-3-oxo-benzofuranone	A	546	445 nm; 517 nm	violet
Example 28/8: Isatin	B	372		brown-red
Example 28/9: 6-Hydroxy-3-oxo-benzofuranone	B	406		red

Example 29:General preparation of lactams of Examples 29/1-6, 3-oxofuranone being replaced in each case in accordance with the table below.:

3-Oxofuranone, 0.01 mol, is dissolved together with 4-ethoxycarbonyl-5-(4-chloro)phenylpyrrolin-2-one (A), 0.01 mol, or 4-ethoxycarbonyl-5-phenylpyrrolin-2-one (B), 0.01 mol, in 50 ml of glacial acetic acid and the solution is boiled under reflux until starting material can no longer be detected. The solvent is evaporated off in vacuo and the residue is washed with a little hexane. The filtrate is left to stand in a refrigerator overnight and then the residue is filtered off with suction and dried in vacuo.

3-Oxofuranone	Product	m/w	Colour	λ_{max}
Example 29/1: 5,7-Di-t-butyl-3-oxobenzofuranone	A	508	claret	517 nm
Example 29/2: 5,7-Di-t-butyl-3-oxobenzofuranone	B	473	violet	
Example 29/3: 5-t-Butyl-7-methoxy-3-oxobenzofuranone	B	447	claret	
Example 29/4: α-Naphtho-3-oxofuranone	B	411	blue	546 nm
Example 29/5: α-Naphtho-3-oxofuranone	A	445	brown	546 nm
Example 29/6: 6-Hydroxy-3-oxo-benzofuranone	A	411	violet	520 nm

Example 29/7: A solution of 5,7-di-tert-butyl-3-oxobenzofuran-2-one, 4 g (15.4 mmol), prepared in accordance with Example 1b, and 1,2-dihydro-4-(4-chlorophenyl)pyrrolone-3-carboxylic acid ethyl ester, 4.46 g (obtainable in accordance with Bull. Soc. Chem. Belg., 97, 8-9, 615, 1988) in 100 ml of acetic acid is boiled under reflux for 17 h. The solvent is subsequently distilled off at 60°C/60 mbar and the product is chromatographed with 3 l of toluene over silica gel (0.025-0.064 mm). This gives 2.96 g of reddish brown powder comprising a compound of the formula (XLIII)



(XLIII)

Example 30:General preparation of pyrazolinones of Examples 30/1-2, 3-oxofuranone being replaced in each case in accordance with the table below:

3-Oxo-furanon, 0.01 mol, and 1-phenyl-3-methyl-5-pyrazolone (ALDRICH), 0.01 mol, are dissolved in 50 ml of glacial acetic acid (synthesis A) or in 50 ml of tetrahydrofuran with the addition of 0.1 ml of conc. hydrochloric acid (synthesis B) and the solution is boiled under reflux until starting materials can no longer be detected. The solvent is evaporated off in vacuo and the residue is recrystallized from methanol and then dried in vacuo.

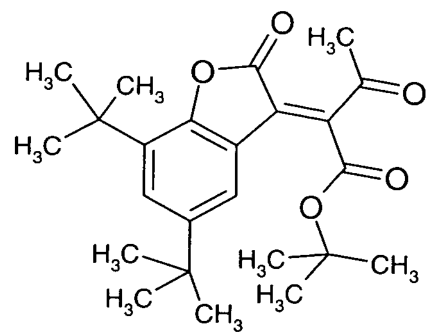
3-Oxofuranone	Product	m/w	Colour	λ_{max}
Example 30/1: 5,7-Di-t-butyl-3-oxobenzofuranone	B	416	violet	517 nm
Example 30/2:α-Naphtho-3-oxofuranone	A	354	red	399 nm

Example 31: Preparation of CH acids of Examples 31/1-2

Example 31/1:

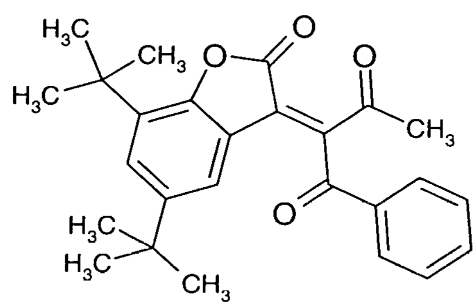
t-Butyl acetoacetate, 0.01 mol, and 5,7-di-t-butyl-3-oxobenzofuranone, 0.01 mol, are dissolved in 30 ml of toluene, 1.3 g of glacial acetic acid and 0.9 g of ammonium acetate are added, and the mixture is boiled under reflux for 8 hours. The solvent is distilled off in vacuo

and the residue is recrystallized from methanol. This gives 0.21 g of orange crystals of a compound of the formula



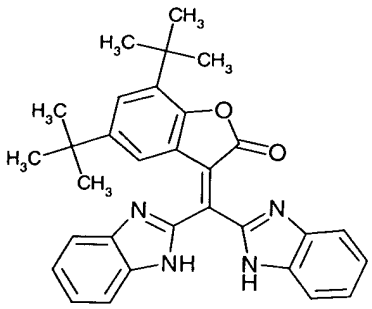
Example 31/2:

Benzoylacetone (FLUKA), 0.02 mol, and 5,7-di-t-butyl-3-oxobenzofuranone, 0.02 mol, are dissolved in 40 ml of toluene, 0.24 g of glacial acetic acid and 0.15 g of ammonium acetate are added, and the mixture is boiled under reflux until starting material can no longer be detected. The organic phase is extracted a number of times with water, the combined organic phases are dried over sodium sulfate and the solvent is evaporated off in vacuo. The coloured residue is extracted with hexane and recrystallized from hexane. This gives 0.52 g of pure, orange product (m/w= 404; λ_{max}= 349 nm; 450 nm) of the formula



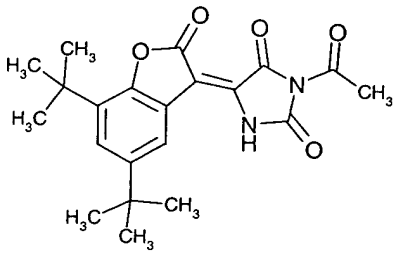
Example 31/3:

Methylenebis(2-benzimidazole), 0.01 mol, in analogy to US 4 225 489, and 5,7-di-t-butyl-3-oxobenzofuranone, 0.01 mol, are dissolved in 30 ml of toluene, 0.001 mol of piperidine is added, and the mixture is boiled under reflux until starting material is no longer present. After cooling, the product is filtered off with suction and recrystallized from ethanol, toluene and then dichloroethane, in each case with the addition of active carbon. This gives 1.10 g of yellow product (m/w= 490; λ_{max}= 420 nm) of the formula



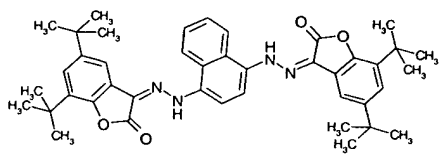
Example 31/4:

Hydantoin (FLUKA), 0.02 mol, and 5,7-di-t-butyl-3-oxobenzofuranone, 0.02 mol, are dissolved in 25 ml of acetic anhydride, 2 mmol of sodium acetate are added and the mixture is boiled under reflux until starting material can no longer be detected. The product is filtered off with suction, washed with methanol and water and dried in vacuo. This gives 1.3 g of monoacetylated product (yellow, m/w= 384; λ_{max}= 391 nm) of the formula



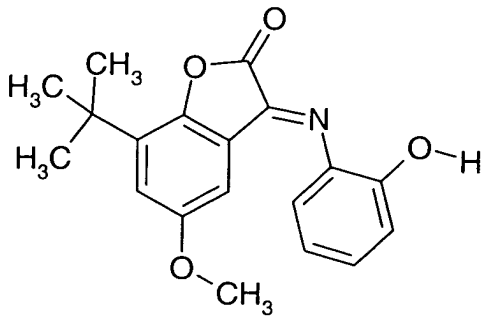
Example 32/1:

1,4-Dihydrazinophthalazine (prepared, for example, in accordance with DE 845200), 0.02 mol, is suspended with 5,7-di-t-butyl-3-oxobenzofuranone, 0.042 mol, in 70 ml of glacial acetic acid (Fluka) and the suspension is boiled under reflux until starting materials can no longer be detected. The precipitate is filtered off at room temperature after the solution, if appropriate, has been concentrated somewhat. The product is washed with methanol and dried in vacuo. This gives a red compound having a molecular weight of 672 m/w



Example 33/1-4:

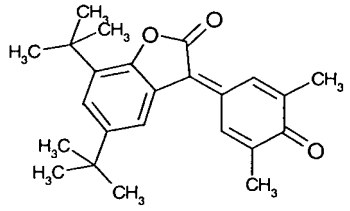
General preparation of 2-hydroxyimines, the 3-oxofuranone and the 2-hydroxyaniline being replaced in each case in accordance with the table below:



The hydroxy aniline (Fluka), 0.02 mol, is dissolved together with 3-oxofuranone (0.02 mol) in 50 ml of glacial acetic acid (Fluka) and the solution is heated at 100°C until starting material can no longer be detected. The precipitate is filtered off with suction or, if appropriate, the solvent is concentrated by evaporation and the residue is recrystallized from glacial acetic acid, if appropriate with the addition of active carbon, and dried in vacuo.

3-Oxo furanone	2-Hydroxy aniline	m/w	Colour	λ_{max}
Example 33/1: 5-t-Butyl-7-methoxy-3-oxo-benzofuranone	2-Hydroxyaniline	325	orange	463 nm
Example 33/2: 5-t-Butyl-7-methoxy-3-oxo-benzofuranone	2-Hydroxy-1-aminonaphthalene	375	red	463 nm
Example 33/3: 5,7-Di-t-butyl-3-oxo-benzofuranone	2-Hydroxy-1-aminonaphthalene	401	orange	412 nm
Example 33/4: β-Naphtho-3-oxofuranone	2-Hydroxyaniline	289	orange	452 nm

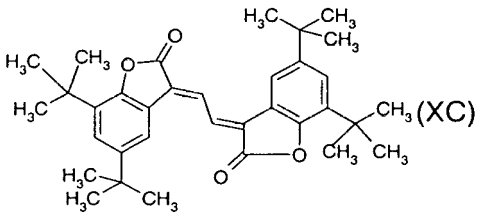
Example 34: Synthesis of a quinomethide



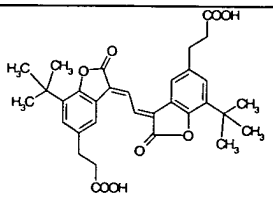
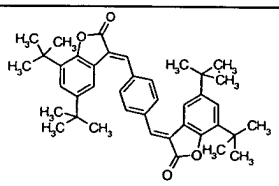
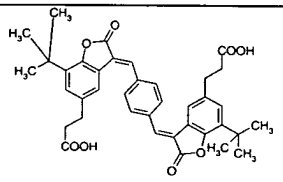
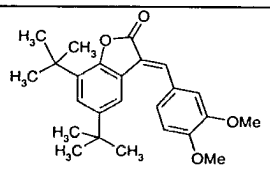
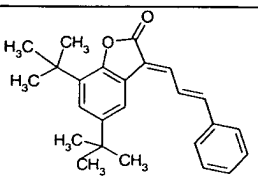
3-(2,5-Dimethyl-4-hydroxyphenyl)-3H-5,7-di-t-butylbenzofuranone, 13.6 mmol, prepared, for example, in accordance with Synlett 1999, S1, pp. 863-864, dissolved in 100 ml of toluene (Fluka) is admixed with 123.5 mmol of potassium hexacyanoferrate(III) (Fluka), 307 mmol of sodium hydroxide (Fluka) and 100 ml of water and stirred at room temperature. When starting material can no longer be detected, the organic phase is separated off, shaken with water and dried over sodium sulfate, and the solvent is removed by evaporation. The residue is recrystallized from isopropanol and dried at 60°C in vacuo. Red crystals are obtained.

Example 35:

A solution of 5,7-di-tert-butyl-3H-benzofuran-2-one, 4.0 g, and 35 ml of acetic acid is heated to 106°C and a 40% aqueous glyoxal solution, 0.94 ml (Fluka purum), is added dropwise to it. The reaction mixture is stirred further overnight. The mixture is stirred at 105°C for 20 hours. Thereafter, the resulting mixture is cooled to room temperature and filtered. The filter residue is washed with acetic acid and then with water, and subsequently dried in a drying oven at 60°C and 200 mbar. This gives 1.0 g of a red powder of the formula (XC)



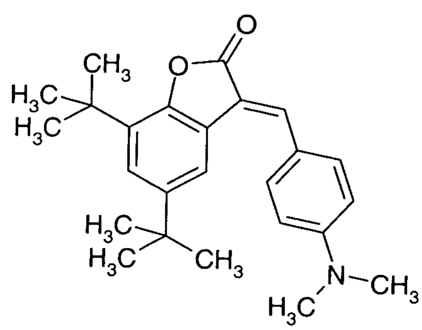
In analogy to the process in Example 35, the compounds of Table 8 are prepared, Example 35b being carried out in the presence of methanol using 10% methanesulfonic acid as catalyst.

Example	Product	Starting materials	Colour
35a	 (XCb)	Glyoxal (FLUKA), 5-t-butyl-7-propionic acid-3H-benzofuran-2-one	orange
35b	(XCb)	see above	orange
35c	 (CCIII)	Terephtal-aldehyde/(FLUKA) 5,7-di-t-butyl-3H-benzofuran-2-one	yellow
35d	 (CCIV)	Terephtal-aldehyde/(FLUKA) 5-t-butyl-7-propionic acid-3H-benzofuran-2-one	yellow
35e	 (CCV)	3,4-Dimethyl-benzaldehyde (FLUKA), 5,7-di-t-butyl-3H-benzofuran-2-one	yellow
35f	 (CCVI)	Cinnamaldehyde (FLUKA) 5,7-di-t-butyl-3H-benzofuran-2-one	yellow

Example 36:

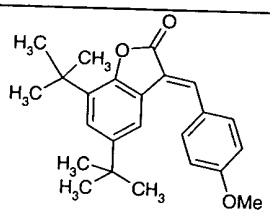
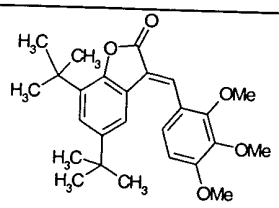
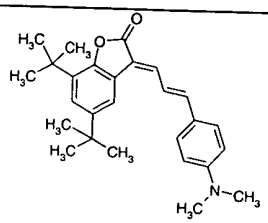
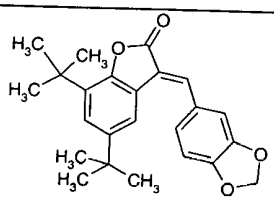
In analogy to the process in Example 1 from EP 0 632 102 the compounds of Table 9 are prepared, or in accordance with the procedure below:

A mixture of 5,7-di-tert-butyl-3H-benzofuran-2-one, 2.0 g, 4-dimethylaminobenzaldehyde, 1.25 g (Fluka puriss) and piperidine, 0.1 ml (Fluka puriss) in 25 ml of toluene is heated at 112°C, the water of reaction being removed simultaneously using a water separator. The reaction mixture is stirred further overnight. The mixture is stirred at reflux for 7 hours. Thereafter, the mixture obtained is concentrated and the residue is treated with 30 ml of methanol. The red solid obtained is filtered, and the filter residue is washed with methanol and then with water and subsequently dried in a drying oven at 60°C and 200 mbar. This gives 1.7 g of a red powder of the formula (CCVII)



(CCVII)

The compounds of Table 9 are prepared in analogy to the above process in Example 36:

Example		Starting materials	Colour
36a	 (CCVIII)	4-Dimethylamino-benzaldehyde (FLUKA), 5,7-di-t-butyl-3H-benzofuran-2-one	yellow
36b	 (CCIX)	2,3,4-Trimethoxy-benzaldehyde (FLUKA), 5,7-di-t-butyl-3H-benzofuran-2-one	yellow
36c	 (CCX)	4-Dimethylamino-cinnamaldehyde (FLUKA), 5,7-di-t-butyl-3H-benzofuran-2-one	violet
36d	 (CCXI)	Piperonal (FLUKA), 5,7-di-t-butyl-3H-benzofuran-2-one	

Example 37:

15 g of vinyl copolymer (with 13% acetate, 86% chlorine and 1% copolymerized maleic acid, e.g. VINYLITE VMCH from UCC) is stirred into 30 g of toluene and 50 g of methyl ethyl ketone and brought into solution completely (dissolver for about 20 minutes or propeller stirred for about 1 hour). Subsequently, 5 g of a lactone dye of the formulae (XLIII-LXXIII) is

incorporated by stirring for 5-15 minutes. The printing ink prepared in this way is applied to aluminium or to metallized polymer films or used as the basis for a hot stamp onto a polyester film.

Example 38: Preparation of injection-moulded plaques in polyethylene terephthalate (PET)

0.3 g of compound of the formulae (XLIII-LXXIII) is mixed with 1500 g of polyethylene terephthalate (PET) [^{TM}MELINAR PURA, ICI, predried at 120°C) briefly by hand, then on a tumble mixer at 50 rpm for 5 min. This mixture is subsequently preextruded at 270°C on a 25 mm single-screw extruder (Collin).

The compound is subsequently processed on a microprocessor-controlled injection moulding machine (^{TM}Ferromatik FM 40, Klöckner). The residence time of the polymer (dependent on cycle time, screw volume and plastification volume) is 5 min, during which backpressure and screw speed are kept low. This is beneficial to the homogeneity of the plastic and prevents the generation of frictional heat. The first mouldings (plaques 65 × 25 × 1.5 mm in size) are discarded.

The mouldings obtained at 270°C, 280°C, 290°C and 300°C are notable for very high heat stability, high light fastness, good migration resistance and high colour strength.